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PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 27th, 1924.

By WILLIAM PALMER WYNNE, D.Sc., F.R.S.

Some Aspects of Russia's Contribution to Chemistry.

THREE years ago the deplorable position in which Russian men of science found themselves placed attracted the attention of the Council of this Society as of other learned bodies. To mitigate the acute distress and poverty revealed by reports from visitors to Russia and in letters received from Petrograd and elsewhere, a fund was raised by means of which food, clothing, books and apparatus were sent out to our colleagues in that unhappy country. It is difficult indeed for us to realise how great is the disaster which has overtaken chemistry in Russia. That some of those whose names were famous before the War are still living—Ipatiev, B. Menschutkin, Zelinski among them—is a matter for rejoicing. By them we may be confident that the high tradition of Russian chemistry will be maintained as time and circumstance permit, but their work of reconstruction, difficult as it must inevitably be from the lack of books, apparatus and materials, is hampered further—so it would seem—by the low level to which education has fallen during the recent difficult years. If the restoration of the standard of educational attainment cannot be otherwise than slow—even under the most favourable conditions—no argument is needed to show that research must be hampered for many years to come. That, I venture to think, is a calamity, for chemistry is international and its development must suffer if for any reason the contribution which a distinctive school like the Russian may make to the treasury of achievement is withheld or withdrawn.

In this country, perhaps in other parts of Western Europe, the appreciation of Russia's contribution to chemistry has suffered from two causes at least. During the fifty years preceding the War, the greater part of the work appeared in Russian journals, but in earlier years, being published in German or less frequently in French, it received less than its due meed of recognition as coming from Russian sources. It has occurred to me, therefore, that some encouragement might be furnished to our sorely tried colleagues if the effort were made to show why chemists must ever be appreciative of the results of Russian research.

Russia from the point of view of cultural development is one of the younger European nations. Her awakening began during the reigns of Peter the Great and the Empress Catherine some two

hundred years ago. How great has been her contribution to music, to literature and to art in its widest sense, since the middle of last century, is admitted by everyone. But if we recognise the distinctive achievement either of the school of music associated with the names of Balakirev, Borodin—himself a chemist—Rimski-Korsakov, Tschaikovski and others, or of writers such as Turgeniev, Dostoievski, Leo Tolstoi and their contemporaries, as something, lacking which the world would be immeasurably poorer, it is no overstatement to assert that the growth of chemistry would have been dwarfed in no less degree had the work of Mendeléev, Butlerov, Wagner, and their successors been withheld from the common stock of knowledge.

In the time at my disposal, any detailed reference to the Universities and Technical Schools in which provision was made for teaching chemistry before the War must perforce be omitted. Nor can I do more than glance at the difficulties under which it was taught for many years, owing to the restricted accommodation of such laboratories as there were until comparatively recent times—three examples will suffice from among many. When Zinin went from Kazan to the Medical Academy at Petrograd in 1848, the annual laboratory grant for chemistry was 30 roubles, a sum rather less than three pounds (£3) in value. Twenty years later, Saytzev began his long tenure of the chair at Kazan, yet the laboratory was still so small that Reformatski, one of his students who wrote his obituary for the Russian Chemical Society, states that turning round in it was considered inadvisable. And in 1886, when Wagner went to Warsaw, his laboratories consisted of two very small and narrow rooms in a basement, from which he did not move until the Chemical Institute of the Warsaw Polytechnic designed by him was ready for occupation in 1902—only a year before his lamented death. To difficulties such as these, not altogether unknown perhaps in bygone days in this country—difficulties which seem to justify the view attributed to Victor Meyer " that the best work has been done in the worst laboratories " —must be added others arising from the repressive measures instituted by the Government after the assassination of the Tsar, Alexander II, on March 1st, 1881; measures which crippled the freedom of intercourse between teachers and students and even between teachers themselves, to the great detriment of progress in learning and knowledge, to provide which is the chief function of a University's existence.

By a strange coincidence, it is to a Tsar of the same name, Alexander I, that Russia owed the enlightened policy that added to the six Universities (including those of Moscow and Petrograd),

which came under Government control at the beginning of last century, three others founded in 1804 respectively in Charkov, Kazan, and Kiev. Of the nine, Kazan from the chemist's point of view is the most interesting as, in its influence on the development of Russian chemistry, it recalls the famous laboratory at Giessen, while K. K. Claus and N. Zinin, its first Professors of Inorganic and Organic Chemistry, were no whit behind Liebig in the enthusiasm they inspired among their students.

The beginnings of Russian chemistry, it is true, have been traced by the younger Menschutkin to M. V. Lomonossov, who lived in Petrograd in the earlier part of the eighteenth century, built a laboratory there in 1749, and was one of the founders of its University. Working at a time when Stahl's phlogiston hypothesis met with general acceptance, Lomonossov anticipated Lavoisier by nearly twenty years in his proof that the increase in weight of tin and lead, when calcined under Boyle's conditions in closed vessels containing air, came from the air and from no other source. But in the study of combustion, as in other fields of inquiry, he had the misfortune to be in advance of his times; his work failed to secure recognition until the beginning of this century, and he left no successor. Therefore it is that Chemistry had to make a fresh start in the years which elapsed between the founding of the University at Kazan and the completion of its chemical laboratory in 1835.

Before the War, Kazan, a town of some 140,000 inhabitants situated about 650 miles east of Moscow and 250 miles below Nijni Novgorod on the Volga, was the intellectual capital of Eastern Russia, and its University was attended by about 1,000 students. Claus, its first Professor of Chemistry, who is best remembered for the discovery of ruthenium in 1846 and for investigations on rhodium, ruthenium and iridium compounds, had been a pupil of Berzelius. Zinin, who entered the University as a student in 1830, at the age of eighteen, became Professor in 1837, spent the next three years in Germany chiefly with Liebig at Giessen, returned to Kazan in 1841 and seven years later was transferred to Petrograd, where he remained until his death in 1880.

Among Zinin's more striking contributions to organic chemistry may be mentioned such fundamental discoveries as the reduction of nitrobenzene to aniline in 1842, of nitronaphthalene to α-naphthylamine in the same year, and of *m*-dinitrobenzene to *m*-phenylenediamine in 1844, the reducing agent in each case being ammonium sulphide. The identity of Zinin's product, named by him benzidam, with aniline from indigo was demonstrated by Hofmann in 1843. Those who recall the late Sir Frederick Abel's account of the

troublesome process by which the aniline required for Hofmann's researches was obtained from indigo in the early 'forties of last century, will appreciate the convenience of the new method. Although soon replaced by agents more rapid in action, when complete reduction is required, ammonium sulphide is still of service in the step by step conversion of polynitro-compounds into amines. To Zinin is due the isolation of azoxybenzene and its conversion by distillation into a mixture of azobenzene and aniline—thus affording an explanation of Mitscherlich's process for preparing azobenzene from nitrobenzene by reduction with alcoholic potash—and, what is even more important, to him is also due the discovery of benzidine, which was achieved by the action of dilute sulphuric acid on the product formed when azobenzene is reduced by hydrogen sulphide. Hofmann later identified this product as hydrazobenzene, but it may be mentioned that Alexiev, then Professor of Chemistry at Kiev, seems to have been the first to devise the modern method of reducing nitrobenzene to hydrazobenzene by means of zinc dust and caustic soda.

Four years before Zinin left Kazan, A. Butlerov entered the University as a student. Looking backward, it seems strange, in view of the important part he was to play in the development of organic chemistry, that he should have been debarred by regulations from attending Zinin's lectures and worked only with Claus—then about fifty years old. On Zinin's resignation, nevertheless, Butlerov succeeded him, at first in a temporary capacity, being given the title of Professor in 1852. Later, in 1857, he went first to Heidelberg, where he met Kekulé, then to Paris to work in Wurtz's laboratory, returning the following year to Kazan imbued with the new ideas about structural chemistry which characterised Western chemical thought in the middle of last century. Thereafter, as one enthusiastic chronicler records, the "Russian Butlerov school of chemistry" quickly made its mark. Despite the crowding inevitable owing to its restricted area, students flocked to the Kazan laboratory, so that to secure admission was accounted a piece of rare good fortune. Later its fame may have been enhanced by the publication of Butlerov's text-book of organic chemistry early in 1864—a book remarkable for its viewpoint even in a remarkable age and deemed worthy of translation into German at a time when Kolbe's and Kekulé's text-books might have been expected to suffice for the needs of German students.

Before the nature of Butlerov's contribution to chemistry is discussed, it will be convenient to have the names of those who followed him in the Chair after his call to Petrograd in 1868. The first is Markovnikov, who went to Odessa three years later and to

Moscow as Professor in 1873; then A. N. Saytzev, who occupied the Chair from 1871 to 1909; and afterwards Flavitzki. To Markovnikov perhaps more than to any of his contemporaries is due the wide adoption of the principle that Russian work should be published only in the Russian language—an adoption rendered the more easy by the foundation of the Russian Chemical Society in 1868. As will be seen, there is a homogeneity about the steady stream of research flowing from Kazan which makes an appreciation of its influence on the progress of chemical knowledge relatively easy. But Petrograd, with its numerous Institutes and the work of its long and distinguished line of professors and teachers, might equally well have been chosen to illustrate the stimulating character of Russian chemical investigation—were it not for the fact that nothing new remains to be said of chemists of the stature of Mendeléev, who long ago joined the immortals, A. N. Menschutkin and Beilstein: their place in chemistry and their achievement are known throughout the world.

The Russian Chemical Society has been mentioned: it reached its Jubilee a week later than Armistice day, the first meeting having taken place on November 6th/18th, 1868, with Mendeléev in the chair. The original members numbered 48, of whom 37 were resident in Petrograd and three in Moscow. Beilstein was elected secretary and Menschutkin treasurer with a committee of three, among whom was Fedorov. Three papers were read at this meeting by Menschutkin, Beilstein and Fedorov, respectively. The first volume, for the year 1869, contained 38 papers, including one, now a classic, by Mendeléev on the relationship between the atomic weights and properties of elements. This volume occupied 264 pages exclusive of index. In 1914, Schroeder being President, Ipatiev secretary and Sokovinin treasurer, the last meeting of the year was held on December 4th with Tschugaev, Vice-President, in the chair, and the volume for that year contained 151 papers, occupying 1952 pages exclusive of index, followed by a report on "the present position of the Russian chemical industries" extending to a further 274 pages. These reports, which began in 1897 with one on "the dye problem in France and Germany," dealt each year with a single subject such as synthetic nitrates, Thiele's theory of conjugation, and so on, and beyond question served a useful purpose as monographs of the current state of knowledge in particular directions. Since the Revolution, parts of the journal have been issued only at long intervals, but there is some ground for hope that the period of greatest depression has passed, as papers of Russian origin are making their appearance with growing frequency in chemical journals.

Let us now turn from these matters of merely general interest to face the question : What is the debt which Chemistry owes to the Kazan school? Stated broadly, it may be said to be the searching scrutiny of the property of unsaturation as manifested on the one hand by hydrocarbons isologous with the paraffins and on the other by carbonyl derivatives. Herein is found an essential difference between the type of investigation pursued by Zinin and that undertaken by his successors.

Butlerov, after his return to Kazan from Germany, studied first of all the interaction of methylene iodide and silver acetate or oxide which furnished a polymeride of formaldehyde, called by him dioxymethylene as the result of an incorrect vapour density determination, but later shown by Hofmann to be trioxymethylene. From it by interaction with ammonia, hexamethylenetetramine (hexamine) was produced and a few months later by means of hot lime-water a substance described as sugar-like but with a bitter taste, to which—on account of its origin and likeness to mannitan—he gave the name methylenitan. The analytical figures quoted indicate the presence of impurity and agree better with the formula $C_6H_{12}O_6$ than with $C_7H_{14}O_6$ which Butlerov adopted. Investigated afresh more than twenty-five years later, this reaction, carried out at the ordinary temperature, was found by Loew and by Fischer to furnish hexose sugars, including α-acrose, while it supplied evidence for Baeyer's well-known view, advanced in 1880, that the photosynthesis of sugar from carbon dioxide and water is achieved through the intermediary of hydrated formaldehyde and is the basis of the constantly renewed efforts to accomplish this synthesis independently of the living plant.

Not unnaturally, as he had worked with Wurtz and met Kekulé, Butlerov took part in the controversies which arose between Kolbe and Kekulé in connexion with molecular constitution, and particularly the constitution of isomerides. He gives reasons why isomerism is not to be expected between compounds such as $\begin{matrix}CHCl_2\\CH_3\end{matrix}$ and $\begin{matrix}CH_3\\CHCl_2\end{matrix}$, whereas $\begin{matrix}CHCl_2\\CH_3\end{matrix}$ and $\begin{matrix}CH_2Cl\\CH_2Cl\end{matrix}$ must be isomeric, and in 1863 comes into line with Gerhardt and others in advocating the abandonment of the paired atoms, which Berzelius in an unhappy moment had introduced into chemistry; he stresses the quadrivalency of carbon; argues the existence of doubly-linked carbon atoms in unsaturated compounds, and among other fruitful suggestions advocates formulæ for acetic acid and succinic acid which, bearing in mind the implications of his symbols, are not to be distinguished from those adopted at the present day.

Kolbe, who in 1860 predicted the existence of secondary and

tertiary alcohols—a prediction confirmed by Friedel's preparation of *iso*propyl alcohol in 1861 and Butlerov's synthesis of *tert.*-butyl alcohol in 1864—held the view that if, as appeared to him to be the case, the three hydrogen atoms of the radical methyl prove to be different in value, the number of possible alcohols must be extraordinarily large. To this view, Butlerov offered strong opposition: he will have nothing to do with the idea that a carbon atom may have valencies with varying activities—only when three compounds of the formula $C_2H_3Cl_3$ have been isolated will he consent to take such a view into account. Later, in collaboration with Ossokin, he investigates the structure of ethylene itself, using glycol iodohydrin which, to his surprise, by interaction with zinc methyl, furnished *iso*propyl alcohol, identified by its conversion into acetone. Thereupon, the question is discussed whether ethylene has the structure $\begin{cases}CH_3\\CH\end{cases}$, or, as seems more probable, there is a change into this form during the interaction. Eventually the conclusion is drawn that change in structure occurs at the moment at which the iodine atom is replaced by the alkyl group—a conclusion confirmed in 1890 by Charon and Paix-Séailles, who showed that this unexpected production of secondary alcohol is due to an Eltekov transformation which furnished acetaldehyde as an intermediate stage in the reaction:

$$\begin{matrix}CH_2I\\CH_2{\cdot}OH\end{matrix} \longrightarrow \begin{matrix}CH_2\\CH{\cdot}OH\end{matrix} \longrightarrow \begin{matrix}CH_3\\CH{:}O\end{matrix} \longrightarrow \begin{matrix}CH_3\\CH(OH){\cdot}CH_3\end{matrix}$$

Incidentally, in 1862, Butlerov discussed the constitution of urea, directing attention to two reactions by which alkylated ureas can be produced, namely, (*a*) the interaction of phosgene with ammonia or amines, (*b*) the interaction of primary and secondary but not of tertiary amines with cyanic acid, and emphasising in the latter case the failure to procure tetramethylurea by the use of trimethylamine. Between the carbamide formula (4) then accepted and the alternative constitution (3) proposed by him

" Cyansäure

als den andern Säuren analog construirt betrachtet — als Carbimid

$$(\overset{(1)}{C^{IV}N'''})'(H\Theta)', \qquad (\overset{(2)}{C^{IV}\Theta''})''(HN'''),"$$

Harnstoff

$$C^{IV}(H\Theta)'(\overset{(3)}{HN'''})''(H_2N)', \qquad (\overset{(4)}{C^{IV}\Theta''})''(H_2N''')'_2 \quad "$$

he does not make a choice, but the paper has this additional interest, that it suggests a relationship between the two forms of

cyanic acid which in modern chemical language would be described as that existing between tautomerides.

No reference to Butlerov would be complete without some account of the important syntheses carried out by him with zinc methyl and zinc ethyl. Although it is to Frankland we owe the discovery of these compounds, it would not be difficult to substantiate the claim, if it were made, that the extensive employment of these synthetical agents which continued until the discovery of the more convenient magnesium derivatives was due largely to the use made of them at Kazan by him and later by Saytzev and his collaborators, among whom were Wagner and Reformatski, afterwards Professor at Kiev.

Butlerov's earliest work with zinc alkyl compounds was concerned with the interaction of phosgene and zinc methyl, leading to the formation of a crystalline compound from which, by means of water, *tert.*-butyl alcohol was unexpectedly obtained. Suspecting either acetone or acetyl chloride to be an intermediate product of the reaction, he was led to study the behaviour of each with zinc methyl. Acetone showed little reactivity, but on repeating Pebal and Freund's work with acetyl chloride and zinc methyl, he obtained *tert.*-butyl alcohol, the reaction being represented thus:

$$\text{“ } \begin{matrix}CH_3\\COCl\end{matrix} + 2\left(\begin{matrix}CH_3\\CH_3\end{matrix}Zn\right) = \begin{matrix}C_4H_9\\CH_3Zn\end{matrix}O + \left[(CH_3)Zn\right]'Cl \text{ ”}$$

The well-crystallised additive product on decomposition with water gave *tert.*-butyl alcohol and marsh gas. Later work by Pavlov confirmed the view advanced by Wagner and Saytzev that the reaction with zinc methyl proceeds in two stages, Butlerov's product being obtained in the second:

$$CH_3{\cdot}CCl{:}O + ZnMe_2 \longrightarrow CH_3{\cdot}CClMe{\cdot}OZnMe$$

$$CH_3{\cdot}CClMe{\cdot}OZnMe + ZnMe_2 \longrightarrow CH_3{\cdot}CMe_2{\cdot}OZnMe + ZnMeCl$$

$$CH_3{\cdot}CMe_2{\cdot}OZnMe + H_2O = CH_3{\cdot}CMe_2{\cdot}OH + MeH + ZnO$$

Hitherto, it had been supposed that chlorine was the reactive part of the ·CO·Cl group and that, for example, acetic acid was formed in the interaction with water by exchange initially of this chlorine atom for hydroxyl. There was additional reason for this view inasmuch as the formation of additive compounds through the intermediary of the carbonyl group, in those cases in which polymerisation is excluded, seemed to require in the addendum at least one atom of hydrogen, with which the oxygen atom of this group could combine to furnish a hydroxyl radical. The existence of this restriction could no longer be maintained in view of the formation of additive compounds with zinc alkyl derivatives. Thenceforward

the production and hydrolysis of esters, acid chlorides, amides and the like could be interpreted as dependent on the unsaturatedness of the carbonyl group, as with additive compounds from aldehydes or ketones. Of all these additive compounds, those with the elements of the water molecule, such as carbonic acid or ethylidene glycol, are so unstable as in most cases to be incapable of isolation. But there are exceptions, as for example glucose hydrate, $C_6H_{14}O_7$, and chloral hydrate, $CCl_3{\cdot}CH(OH)_2$, although these can be rendered anhydrous without difficulty. It is to Petriev of Odessa that we owe the discovery of the first compound in which the $>C(OH)_2$ group does not lose the elements of water at temperatures below those at which complete decomposition occurs—mesoxalic acid was assigned the formula $C(OH)_2(CO_2H)_2$ by him in 1874 and his view of its structure and that of its salts received support by the isolation of dihydroxytartaric acid, $C_2(OH)_4(CO_2H)_2$ fifteen years later.

On reduction, acetone yields the glycol pinacol as minor product from which pinacolin is obtained by dehydration. This transformation was first observed by Fittig (who did no more than analyse the product and make a dichloro-derivative), but the constitution of pinacolin was established by Butlerov, who synthesised it from trimethylacetyl chloride, $CMe_3{\cdot}COCl$, and zinc methyl and that of pinacol by Pavlov, who obtained it from tetramethylethylene dibromide, $CMe_2Br{\cdot}CMe_2Br$ (by conversion into the acetate and saponification with baryta). The dehydration of pinacol achieved by weak acids involves the exchange of a methyl and a hydroxyl group between contiguous carbon atoms :

$$CMe_2(OH){\cdot}CMe_2{\cdot}OH \longrightarrow CMe_3{\cdot}CMe(OH)_2 \longrightarrow CMe_3{\cdot}CMe{:}O + H_2O$$

and it may be noted that Zelinski and Zelikov have shown that the methyl group may be retransferred by distilling pinacolin alcohol, $CMe_3{\cdot}CMeH{\cdot}OH$ (obtained from pinacolin by reduction with sodium amalgam) with anhydrous oxalic acid, a process also involving dehydration :

$$CMe_3{\cdot}CMeH{\cdot}OH \longrightarrow CMe_2(OH){\cdot}CMe_2H \longrightarrow CMe_2{:}CMe_2 + H_2O$$

Many examples of this type of change are now known—the Beckmann change characteristic of ketoximes belongs to the same category—and among them, as reference is made later to tri*iso*-butylene and bornylene, may be quoted the conversion of the former into methyldibutylacetic acid by oxidation in acid solution which Frl. Lermontov, one of Butlerov's pupils, explains thus :

$$C(CMe_3)_2{:}CMe_2 + O + H_2O \longrightarrow C(CMe_3)_2(OH){\cdot}CMe_2{\cdot}OH \longrightarrow$$
$$CMe(CMe_3)_2{\cdot}CMe(OH)_2 \longrightarrow CMe(CMe_3)_2{\cdot}CMe{:}O + H_2O \longrightarrow$$
$$CMe(CMe_3)_2{\cdot}CO_2H$$

and of the latter into camphene. Nevertheless, despite many speculations, among which those of Meerwein and his collaborators are the most recent, it is doubtful whether our knowledge of the mechanism of the reaction is much greater than at the time when it was first studied.

Polymerisation also engaged Butlerov's attention and the current explanation of the course of the reaction among olefines is due to him. It was on record that reactions which might be expected to furnish methylene gave rise to ethylene. Butlerov, having confirmed this experience, found that whereas propylene together with two of the isomeric butylenes showed no tendency to undergo polymerisation, *iso*butylene, obtained from *tert.*-butyl alcohol by interaction with sulphuric acid under certain conditions, was accompanied by *two* isomeric di*iso*butylenes to which the formulæ $CMe_2{:}CH{\cdot}CMe_3$ and $CH_2{:}CMe{\cdot}CH_2{\cdot}CMe_3$ were assigned. He had already found *iso*butyric acid in small amount among the oxidation products of *tert.*-butyl alcohol and in explanation of the anomaly had made the suggestion that its origin might be traced to *iso*propylcarbinol formed through the intermediary of *iso*butylene :

$$CH_3{\cdot}CMe_2{\cdot}OH \rightleftharpoons CH_2{:}CMe_2 \longrightarrow OH{\cdot}CH_2{\cdot}CMe_2H.$$

If this explanation be accepted, a modification of one of Markovnikov's rules becomes necessary (*v.* p. 1008), since obviously the additive reaction is not confined to one only of the alternative modes of addition. Here it should be remembered that Michael's experimental proof that both of the additive products are obtained in reactions of this type was not given until twelve years later. Transferred to the case under investigation, *viz.* the production of two di*iso*butylenes, the abrogation of Markovnikov's rule would admit of the reactions involved being represented as follows :

$$CMe_3{\cdot}CH{:}CMe{\cdot}CH_3 \underset{}{\overset{H_2O}{\rightleftharpoons}} CMe_3{\cdot}CH_2{\cdot}CMe(OH){\cdot}CH_3 \overset{H_2O}{\rightleftharpoons}$$

(chief product)

$$CMe_3{\cdot}CH_2{\cdot}CMe{:}CH_2 \overset{H_2O}{\rightleftharpoons} CMe_3{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}OH$$

(minor product)

But Butlerov's vision is wider than this. A careful study of the reaction leads him to suggest that in the polymerisation equilibrium is set up between the di*iso*butylenes, the alcohols into which they can be converted or from which they may be formed, and water, and to add the still more striking conjecture that while the presence of sulphuric acid is necessary for the conduct of these reactions, equilibria may exist in the absence of any reagent : thus, hydrogen cyanide may be regarded as an equilibrium mixture of nitrile and

carbamine. Here he harks back to the ideas about cyanic acid and carbimide already mentioned in connexion with urea (*v.* p. 1003). It is not difficult to find in these suggestions of duality of structure an anticipation of that idea of tautomerism which ten years later was to introduce into chemistry a fertile source of controversy and research.

Among Butlerov's first students after his return to Kazan was W. W. Markovnikov, who entered for a course in political science but soon abandoned it for chemistry. Within nine years, and before going to Germany to gain additional experience, Markovnikov, doubtless as the result of fruitful intercourse between teacher and student, published in 1865 a book of which, according to Decker, the title (translated) ran "The influence which the Atoms in a Molecule exert on one another." The book, published in Russian, has never been translated and its existence seems to have been unknown outside that country until Michael, in the paper already mentioned, quoted from it. At a time when chemical theories of structure were being rapidly developed from those advanced by Gerhardt to those dependent on valency and associated with names such as Frankland, Kekulé and Kolbe, it is significant of an independent judgment that Markovnikov in this book should have emphasised the fact that such theories

> i. do not afford a clue to the particular hydrogen atom in a hydrocarbon which will be displaced by a substituent;
>
> ii. do not indicate which of the two isomerides will be formed by the addition of a halogen hydride to an unsaturated hydrocarbon; or
>
> iii. do not suggest which of the two possible isomerides will be formed by the elimination of the elements of the halogen hydride from neighbouring carbon atoms.

He drew the conclusion that the directing influence in these reactions must be assigned to the atoms remaining in the molecule, and although he put forward certain rules, deduced from observation, which—modified from time to time—have served a useful purpose, he recognised that to solve completely the problem—to fix in what manner and in what direction this influence is exerted—much work would have to be done. In our own time, partial valencies, residual affinities, strain hypotheses, have been invoked, the material accumulated almost baffles comprehension, but the solution of the problem is not yet in sight. Was he not right to insist that, the structure of the molecule having been elucidated, the systematic study of the functions of individual atoms which, although written alike in formulæ, yet in reality behave differently

is the fundamental problem in organic chemistry? How large an expenditure of time and effort such a systematic study may involve can be surmised from Michael's critical examination of Markovnikov's rule about the formation of additive compounds.

As originally stated, this rule asserts that in the combination of a halogen hydride with an unsaturated hydrocarbon having carbon atoms unequally hydrogenated, the " electronegative " constituent attaches itself to the least hydrogenated carbon atom. But Michael's results show that both of the possible isomerides are formed, although in very different proportion, so that the rule is only approximately true. By the introduction of a " positive-negative " hypothesis, Michael supplied what Markovnikov had sought but failed to find, and by its aid assigned to each carbon atom in a chain its influence on the reactivity of a given radical, whence we come by easy stages to Flürscheim's hypothesis and the theories of induced alternate polarities. Nevertheless, these developments, although helpful in many directions, have not solved one, at any rate, of the riddles known to workers in the Kazan laboratories—the riddle which asks: Why does vinyl bromide, uniting with hydrogen bromide, furnish either ethylene or ethylidene dibromide according to the conditions, but vinyl iodide with hydrogen iodide yield only ethylidene di-iodide?

$$\begin{array}{l} CH_2Br \\ CH_2Br \end{array} \longleftarrow \begin{array}{l} {}^{+}CH_2 \\ {}^{-}CHBr \end{array} \longrightarrow \begin{array}{l} CH_3 \\ CHBr_2 \end{array}$$

Similar difficulties are encountered in the chloro- and bromo-propylene series, and Markovnikov's suggestion that in such cases the " negative element of the acid " will place itself alongside the " negative " radical already present in the molecule at low temperatures but in the opposite way when the temperature is comparatively high, is much too definite. Besides furnishing no reason for this type of reaction, it leaves out of account the failure to obtain similar additive compounds with vinyl chloride. As the recent discussion between Professors Lapworth and Robinson and Sir J. J. Thomson in the correspondence columns of *Nature* shows, the interest attaching to the problem is by no means exhausted.

Markovnikov in his first paper described the production of allylene from propylene dibromide but did not break fresh ground, although the hydrocarbon was new. By the preparation of *iso*butyric acid, which was announced before he went to Germany in 1865, he supplied the first example of isomerism in the acetic series. Later he abandoned this field of work, directing his attention when Professor at Moscow almost entirely to an investigation of the group of

saturated cyclic hydrocarbons called naphthenes, C_nH_{2n}, discovered by him in Caucasian oil. In the separation of these hydrocarbons from those belonging to the paraffin, olefine and benzene series, endless time and patience were needed. As fractionation alone was insufficient, however persistently pursued, chemical methods had to be devised and the results checked from time to time by the synthesis of naphthenes from *cyclo*ketones, aromatic hydrocarbons and terpenes, as achieved initially by Wreden at Petrograd in the case of benzene. Incidentally, but only after a long period of uncertainty, the change in structure which may occur when cyclic compounds are reduced by hydriodic acid was discovered as the outcome of the conversion of suberyl iodide into methyl*cyclo*hexane by this method of reduction

$$\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}\!\!>\!CHI \longrightarrow \begin{matrix}CH_2\cdot CH_2\cdot CH\cdot CH_3\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}.$$

Eventually Wreden's hexahydrobenzene, identified in the Moscow laboratory as methylpentamethylene by Kijner, afterwards Professor at Tomsk, was shown to be identical with the naphthene of the same carbon content from Caucasian oil, and later work made it evident that hydriodic acid at high temperatures not infrequently brings about a similar conversion of 6- or 7- into methyl-5- or 6-membered rings. The whole investigation, including the nitration work with which Konovalov's name is associated, is a model of well-designed inquiry. Towards its close, when discussing cases of isomerism which had arisen, Markovnikov recalls the statement made by him in 1869 to the effect that a hydrogen atom attached to a tertiary carbon atom is more easily displaced than that of a methylene or methyl group. Clearly, then, the inciting or restraining influences, to which his rules of addition and substitution bear testimony, were never absent from his mind. Nor would this account of his theorising be complete if reference were omitted to his support for the diagonal formula for benzene, which later found—at least for a time—an advocate in Baeyer on the more secure basis of experimental study.

Markovnikov was succeeded at Kazan by A. N. Saytzev, who entered the University as a student in 1862, coming under Butlerov's influence, and published his first paper in 1864. Going abroad to work with Kolbe and with Wurtz, he returned in 1865 to Kazan, where the remainder of his life was spent. Much of Saytzev's research work was concerned with the systematic synthesis of alcohols, saturated or unsaturated, by the aid of zinc alkyl compounds—thus with Wagner in 1874 he devised a method for the preparation of secondary alcohols from ethyl formate; with others of his

students obtained tertiary alcohols with one or more allyl radicals present in the molecule, from which by oxidation hydroxy-acids were produced; and found that, while ketones having a methyl group in association with the carbonyl radical are inactive, those with larger alkyl groups furnished tertiary alcohols without difficulty. Among those of his investigations in which zinc alkyl compounds had no part, his effort to determine the position of the double linking in the oleic acid molecule should not be overlooked.

Of Saytzev's students, G. Wagner was undoubtedly the most brilliant. He entered Kazan University in 1866 with the view of training for a political career, but coming under Saytzev's influence soon abandoned it for chemistry, as did Markovnikov before him. In 1875 he went to Petrograd and, encouraged by Butlerov, extended Saytzev's method for preparing secondary alcohols by substituting aldehydes of various types, aromatic or non-aromatic, for ethyl formate, thereby obtaining material for the production of ketones with which to test the validity of Popov's rule for the oxidation of this type of compound. Popov's rule as originally devised stated that oxidation proceeded in such a way that the carbonyl group of the ketone remained in association with the smaller alkyl group, for example :

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3 + 3O \longrightarrow CH_3{\cdot}CH_2{\cdot}CO_2H + CH_3{\cdot}CO_2H.$$

But later investigations due largely to Wagner have shown that the products depend on the nature of the radicals. If both are primary, then all the four possible acids are obtained, but if one of them is secondary it is separated and oxidised to the ketone, and if it is tertiary the carbonyl group remains associated with it to furnish the tertiary acid—moreover, the temperature at which oxidation proceeds is not without influence on its course.

Following up this investigation of the scission of the carbon chain in ketones effected by oxidising agents, Wagner turned his attention to the oxidation of unsaturated compounds of the olefine type, which according to the view then accepted led directly to the rupture of the carbon chain at the double bond. By substituting permanganate in dilute neutral solution for the nitric acid, dichromate mixture or chromic acid hitherto employed and using it in such proportion that 1 at. of oxygen was supplied for each double linking present in the molecule of the unsaturated compound, he was able to show that the initial step in the oxidation is the formation of a glycol :

$$CH_2{:}CH_2 + O + H_2O = CH_2(OH){\cdot}CH_2(OH),$$

the double linking giving place to a single bond. Breaking of the chain at a point between the carbon atoms thus hydroxylated

occurs as the result of oxidising further the hydrogen atoms associated with them to hydroxyl groups. Incidentally, a new reagent was thus discovered for the qualitative recognition of unsaturated linkings in carbon compounds.

The light thus thrown upon the course of oxidation in the olefine series, supported as it was by a convincing body of evidence, enabled Wagner on the one hand to supply an interpretation of the course of the reaction between fused caustic alkali and acids of the oleic series and on the other to assign structural formulæ to the more important members of the terpene group. Accepting as decisive Limpach's isolation of pelargonic and azelaic acids from the product obtained by oxidising stearolic acid, Wagner assigned to oleic acid the formula $C_8H_{17}\cdot CH{:}CH\cdot C_7H_{14}\cdot CO_2H$, anticipating by several years the confirmatory evidence furnished by Baruch, Edmed and Harries respectively. To account for the production of palmitic and acetic acids in the fusion with caustic alkali, he invoked two types of change: first, an oxidising action at the expense of atmospheric oxygen whereby the glycol

$$C_8H_{17}\cdot CH(OH)\cdot CH(OH)\cdot C_7H_{14}\cdot CO_2H$$

is produced, and secondly the simultaneous oxidising and reducing action known to characterise the behaviour of caustic alkali under favourable conditions, whereby the β-ketone $C_{15}H_{31}\cdot CO\cdot CH_2\cdot CO_2H$ is formed, which subsequently undergoes disruption by hydrolysis, furnishing palmitic and acetic acids.

Overlooked or forgotten, this view that oxidation of an acid, such as stearic or oleic acid, occurs in the β-position thereby rendering possible the successive shortening of the carbon chain by two units at a time, was put forward sixteen years later by Knoop in explanation of the katabolism of fatty acids in the animal body, and is known to physiological chemists as Knoop's theory of β-oxidation. Dakin's interesting observation, corroborating this theory, that β-hydroxybutyric acid and acetoacetic acid are successively formed when butyric acid is oxidised by hydrogen peroxide is a striking testimony to Wagner's prescience.

From these studies of the limited oxidation of unsaturated compounds of the aliphatic series, Wagner, having shown that benzene and its allies do not furnish glycols, turned to investigate the behaviour of unsaturated hydrocarbons of the terpene group towards permanganate, obtaining from limonene the tetrahydroxy-derivative $C_{10}H_{16}(OH)_4$ and from camphene the glycol $C_{10}H_{16}(OH)_2$. These compounds were the first-fruits of that intensive cultivation of the field of terpene chemistry which occupied the last twelve years of his life, and enabled him to assign to pinene, terpineol,

dipentene, bornyl chloride, bornylene and camphene structural formulæ too well known to need reproduction here—formulæ that have survived the test of criticism and by general assent afford the best representation of their properties and relationships. Such an achievement at a time when chemists no less renowned than Tiemann, Wallach and Baeyer were actively engaged in terpene chemistry is a measure not only of Wagner's capacity for work but of his insight, without which mere industry and perseverance are of little avail.

It must not be supposed from this account of the work of the Kazan school of chemistry that the study of hydrocarbons was confined in Russia only to the chemists who have been named. On the contrary, in Petrograd and Moscow from the 'eighties onwards, this type of research attracted, among others, Favorski, Ipatiev and Zelinski, to whose numerous publications the decennial indexes of our Journal bear witness. Favorski is remembered more especially for his recognition of the remarkable alteration in structure which hydrocarbons homologous with allylene undergo when heated with alcoholic caustic alkali—a change reversed by interaction with sodium :

$$CH_3{\cdot}CH_2{\cdot}C{:}CH \rightleftharpoons CH_3{\cdot}C{:}C{\cdot}CH_3;\ (CH_3)_2{\cdot}CH{\cdot}C{:}CH \rightleftharpoons (CH_3)_2C{:}C{:}CH_2;$$

Zelinski for his researches on *cyclo*paraffins and olefines and Ipatiev for his production of isoprene by a method which afforded the first clear evidence for the constitution of this important "intermediate" in the synthesis of caoutchouc. Ipatiev also studied the isomeric changes which occur among unsaturated hydrocarbons obtained by the catalytic dehydration of alcohols with hot aluminium oxide, of which the conversion of the amylene $CMe_2H{\cdot}CH{:}CH_2$ into its isomeride $CMe_2{:}CH{\cdot}CH_3$ at 530° may be quoted as an example. Finally, reference must be made to Kutscherov's discovery that hot dilute solutions of mercuric salts convert hydrocarbons of the acetylene series rapidly and almost quantitatively into aldehydes and ketones, thus opening the way to the industrial production of acetic acid from carbide.

In this survey, limited of necessity by the time at disposal, whole sections of Russian chemical work have been omitted. The Petrograd school has already been mentioned. Its earliest achievement seems to have been the discovery of ordinary quinone by Woskressenski in 1838, to which the peroxide formula was assigned; it supplied in Wischnegradzki one of the few Russian chemists who have investigated alkaloids, and as the outcome of Wroblewski's study of the bromotoluidines it made a definite contribution to our knowledge of the structure of benzene. At Riga and Helsingfors

vigorous schools of chemistry flourished before the War. Like Warsaw, they have ceased to be Russian, but the renown of men such as Walden, Aschan and Komppa, and the interest aroused by their work make any detailed reference to them unnecessary. Space can be found only for the mention of one other name, that of A. von Lebedev, whose researches on alcoholic fermentation mark a distinct advance in biochemistry.

Whether, owing to the impoverishment of the country, the endeavour to secure publication of Russian work in Russian which met with much success before the War can be maintained is more than doubtful. It may have to be abandoned temporarily. But whether this prove to be the case or not, the handicap imposed by the language frontier during the last half century or more has not made for progress. Will not those of us therefore who are young enough to take up a foreign language resolve to learn sufficient Russian to enable them to search that treasure house—the Journal of the Russian Chemical Society? There are perhaps two other inducements for this suggestion to be followed—one sentimental in that the first Russian Grammar was compiled by Lomonossov, and the second practical, in that instruction in Russian can now be obtained in all British Universities and in many schools as well.

And one last word. What shall be our message to our colleagues on whom has fallen the task of reconstruction amid unexampled difficulties? After the French Revolution, what was the attitude towards science, towards chemistry and physics in particular, which the Government under the First Consul found itself compelled to adopt if France was to maintain her position among the nations? Was it not an attitude which stimulated and encouraged research, leading directly to the high estimation in which French science was held from the beginning of last century? Confident that in this respect history will repeat itself, let us say with sympathy and admiration for those who are carrying on the good work, that we look forward to the time when their nation will again play a part in the advancement of chemistry no less vigorous and distinguished than was the case before the War.

CXVI.—*The Reaction between Phosphorous Acid and Mercuric Chloride.*

By Alec Duncan Mitchell.

The reaction between phosphorous acid and mercuric chloride has been the subject of several researches, and the various conclusions have been very different. Montemartini and Egidi

(*Gazzetta*, 1902, **32**, ii, 182) concluded that the reaction was of the third order in very dilute solution, but their velocity coefficients were by no means constant. They did not attempt to trace the cause of the deviations from constancy, and their experimental results were so erratic that they probably attributed to experimental error the fact that the curve plotted therefrom is nearly linear over a considerable range. A " lag " in the precipitation of mercurous chloride, which they observed, has not been noticed by any other author. Garner, Foglesong, and Wilson (*Amer. Chem. J.*, 1911, **46**, 361) found that the reaction was quadrimolecular, but it was pointed out by the abstractor (Bray, *Chem. Abs.*, 1912, **6**, 17) that they had applied a formula which requires that both reactants should be present in equivalent proportions, whereas this requirement was not fulfilled in their experiments. Garner (*ibid.*, 648) acknowledged the justice of this criticism and promised to publish re-calculations, but these have not yet appeared. Linhart (*Amer. J. Sci.*, 1913, [iv], **35**, 353) found the reaction to be unimolecular with regard to phosphorous acid, the mercuric chloride functioning as the square root of its concentration, a behaviour which was attributed to the complex $H_2Hg_2Cl_6$, other possible complexes being inactive, but this hypothesis does not account for reactions in which hydrochloric acid is not present initially. He and Adams (*J. Amer. Chem. Soc.*, 1917, **39**, 948) subsequently gave reasons for supposing that the mercuric chloride was reduced to the metal, which reacted instantly with more mercuric chloride to give mercurous chloride. Purkayostha and Dhar (*Z. anorg. Chem.*, 1922, **121**, 156) studied the same reaction and concluded that it was bimolecular for phosphorous acid and semi-molecular (compare Linhart) for mercuric chloride, but they carried out only a few experiments, as their main object was the investigation of the induction of the reaction.

In studying the parallel reaction between phosphorous acid and iodine (J., 1923, **123**, 2241), the author drew attention to the fact that the course of many reactions is obscured by the application of the process of integration to results which do not justify it, and that marked drifts in the course of a reaction may be almost entirely without effect on an integrated velocity coefficient. A review of the work cited above showed that in no case was the indiscriminate use of integration warranted, and it seemed probable that the use of velocity differentials might aid the elucidation of the reaction, especially in view of certain new facts with regard to phosphorous acid which were discovered in its reaction with iodine. These facts were, briefly, that the acid is capable of a reversible change into a second form, and that it may react in virtue of both forms simultaneously.

A few preliminary experiments in which nitric acid or sodium chloride was used in conjunction with hydrochloric acid to vary either the concentration of hydrogen-ions or that of chloride-ions independently of each other, showed that chloride-ions depressed the velocity and that, within limits (see p. 1018), hydrogen-ions accelerated it. Linhart had used only hydrochloric acid and therefore was unable to discriminate between the effects of the two ions. His conclusions as to the function of hydrochloric acid are thus irrelevant and founded upon a superficial examination of the facts.

In order to test the hypothesis developed in the case of the iodine reaction, it was necessary to devise several series of experiments under selected conditions. The clue to the behaviour of the phosphorous acid is to be found by tracing the variations of reaction velocity in relation to the concentration, not of the acid itself, but of the mercuric chloride. For various reasons, none of the data published with regard to this reaction were suitable for such a critical examination, those of Linhart, for instance, being concerned chiefly with changes in the concentration of the hydrochloric acid and involving only comparatively small changes in the concentrations of the other reactants. An important series (III) was that with $M/11$-phosphorous acid and $N/2{\cdot}2$-hydrochloric acid, the initial concentrations of mercuric chloride varying from $M/200$ to $M/6$, and it afforded an extremely good verification of the hypothesis. It was shown, when studying the reaction between hypophosphorous acid and iodine (Mitchell, J., 1920, **117**, 1324), that if only the second form of the acid reacts with the iodine, and if the attainment of equilibrium between the two forms is accelerated in both directions by hydrogen-ions, the assumption requires an expression of the type

$$(ds/dt)(1 + k_5h/a) = k_2hl \quad . \quad . \quad . \quad . \quad . \quad (1)$$

s being the amount of phosphorous acid oxidised in the time t, h, l, and a being the concentrations of hydrogen-ions, phosphorous acid, and mercuric chloride respectively, and k_2 and k_5 being constants (see p. 1024). All concentrations are in moles per litre, and time is expressed in hours. For initial velocities, h is constant throughout this series, and the expression can be written

$$ds/dt(1 + r_1/a) = r_2l;$$

for six experiments in which a varied from 0·159 to 0·0045, the results could be closely represented by constant values of 0·0208 and 0·0222 for r_1 and r_2 respectively.

The reason for the partial success of the assumptions of Linhart and of Purkayostha and Dhar is now apparent. These authors assumed the velocity to vary as the square root of the mercuric chloride concentration; this assumption requires an expression of

the type $ds/dt = rl\sqrt{a}$, and, as may be seen from the initial velocities, v_0, in experiments of this series, this holds fairly well within the range 0·0091 — 0·0364 for a if $r = 0·0730$, but breaks down outside this range (Table I). The experimental error on the initial velocity is of the order of 2 or 3 per cent.

TABLE I.

Expt.	a.	$10^6 \times v_0$.	$10^6 \times 0·0730 \times l\sqrt{a}$ (old formula).	$\frac{10^6 \times 0·0222\, l}{1+0·0208/a}$ (new formula).	Deviation per cent. Old.	New.
T	0·00455	360	449	363	24·7	0·8
G	0·00909	630	633	616	0·5	2·2
H	0·01818	925	898	943	3·0	1·9
I	0·03636	1260	1268	1286	0·6	2·0
J	0·0909	1660	2004	1646	20·7	0·8
W	0·1591	1810	2652	1789	46·5	1·2

Similarly, any other value which might be chosen for r would hold only over a limited range: thus, if r be chosen to give an average deviation of zero, the positive deviations range from 5 to 29 per cent. and the negative from 12 to 15 per cent.

The two expressions under discussion are identical when $rl\sqrt{a} = r_2 l/(1 + r_1/a)$, or, substituting values for r, r_1, and r_2, when $a = 0·011$ or 0·040, these being the roots (other than zero) of the equation. This corresponds with the range indicated and differences between the two expressions are small within this range, but increase rapidly outside it. If Purkayostha and Dhar or Linhart had worked over wider ranges of concentration, they would have noticed the failure of their expression, and, as has been previously mentioned, the process of integration gave a false appearance of validity to the erroneous expression owing to the fact that considerable deviations in the later stages of an experiment do not carry much weight in an integrated constant. This may be shown graphically by a consideration of, for example, a unimolecular reaction. If, as is usual, time is plotted against amount changed (s), considerable deviations in the later stages of the curve have only a small effect on the total area which represents s/k, this area being bounded by the s-axis, the s-asymptote, the moving t-ordinate, and the curve itself, k being the velocity coefficient.

In further support of this hypothesis, it may be mentioned that experiment W gives a unimolecular velocity coefficient for phosphorous acid alone while the concentration of mercuric chloride is decreasing from 0·1591 to 0·0727 * (Table II), thus indicating

* The differential velocity curve falls after this stage, but the integrated velocity coefficient shows no fall till after the next determination. In this particular table, variation of hydrogen-ions is ignored: if this is taken into account, the fall in the value of the velocity coefficient is noticeable at an earlier stage.

that the measurable reaction concerns only the phosphorous acid, since the mercuric chloride is not in excess but is actually in a stoicheiometric deficiency. Obviously, therefore, a necessary antecedent of reaction is a re-arrangement or activation of the phosphorous acid molecule, and the rate of reaction is limited by the maximum rate at which this can take place. As the concentration of mercuric chloride falls, the reaction in which it takes part becomes slower and affects the measurable rate of reaction. All the evidence supports the conclusion that the function of the mercuric chloride is unimolecular in the reaction concerning it. One can therefore postulate the reactions (I) and (II), in which (I) is always of measurable dimensions, whereas (II) is comparatively fast if mercuric chloride is in considerable concentration:

$$H_3PO_3 \text{ (normal form)} \rightleftharpoons H_3PO_3 \text{ (second form)} \quad . \quad . \quad \text{(I)}$$

$$H_3PO_3 \text{ (second form)} + HgCl_2 + H_2O = Hg + H_3PO_4 + 2HCl \text{ (II)}$$

assuming, with Linhart, that these are followed instantly by

$$Hg + HgCl_2 = Hg_2Cl_2 \quad . \quad . \quad . \quad . \quad \text{(III)}$$

TABLE II.

t.	s.	$a-2s$.	$l-s$.	Unimolecular coefficient for $l-s$.
0	—	0·1591	0·09110	—
1·05	0·00187	0·1554	0·08923	0·0197
2·2	0·00382	0·1515	0·08728	0·0194
3·5	0·00610	0·1469	0·08500	0·0198
4·85	0·00825	0·1426	0·08285	0·0196
6·65	0·01134	0·1364	0·07976	0·0200
8·85	0·01485	0·1294	0·07625	0·0201
14·4	0·02282	0·1135	0·06828	0·0200
19·3	0·02940	0·1003	0·06170	0·0201
24·2	0·03487	0·0894	0·05623	0·0199
32·0	0·04321	0·0727	0·04789	0·0201
44·2	0·05350	0·0521	0·03760	0·0200
64·2	0·06424	0·0306	0·02686	(0·0190)

This series is, however, a special case, inasmuch as the high concentration of hydrogen-ions not only emphasises the reactions (I) and (II), but also represses another reaction, and moreover, the high concentration of chloride-ions also represses a further reaction. These obscured reactions can be detected under other definite conditions.

When no extraneous chloride-ion is present initially, the reaction is extremely rapid, but falls off very quickly as chloride-ions accumulate in the course of the reaction; thus, in experiment N, where only $HgCl_2 = 0{\cdot}1818$ and $H_3PO_3 = 0{\cdot}0911$ are present initially, the amounts of mercuric chloride reduced in successive periods of $\frac{1}{2}$-hour are 0·00390, 0·00188, 0·00144, and 0·00114 moles per litre,

although the decrease in concentration of these two reactants during the whole 2 hours is less than 5 per cent., the increase in hydrogen-ion concentration being about 10 per cent. The only ionic or molecular species which alter greatly during this time are the chloride- and $HgCl^{\cdot}$-ions, and the rapid reaction is attributed to the latter, since it is the only possible constituent which could be so sensitive to the increase of chloride-ions, the precise extent of which is shown in Table VI. Also, since reaction is faster than the possible rate of formation of the second form of phosphorous acid, it must be due to the normal form. Thus one has

$$H_3PO_3 \text{ (normal form)} + HgCl^{\cdot} + H_2O \longrightarrow Hg + H_3PO_4 + 2H^{\cdot} + Cl' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(IV)}$$

If the reaction is conducted in the presence of sufficient sodium acetate to neutralise mineral acid, it becomes of quite a different order of velocity. For instance, $M/55$-mercuric chloride and $M/11$-phosphorous acid with approximately $N/2$-sodium acetate and $N/12$-acetic acid give 96 per cent. of the total reaction within 9 minutes, whereas in the presence of hydrogen-ion concentrations of the order of $N/10$ this extent is not attained in less than 24 hours. This is definite evidence of a reaction which is obscured under other conditions. It will be referred to as reaction (V) and is analogous to one of the reactions between phosphorous acid and iodine which has been shown to be due to the normal form of phosphorous acid and predominates in weakly acidic solutions.

A further reaction can be detected by an examination of curves derived from experimental results (Figs. 1 and 2). If v/l is plotted as ordinate, v being the velocity ds/dt, against a as abscissa, the slight branches from the main curve for any one series show that an experiment which has just been started has a lower value for v/l than a similar one having all other conditions comparable but which is already in progress. In the curves each experiment is represented by a full line only over a range such that the concentration of hydrogen-ions has not changed beyond a limit of 10 per cent.; a broken line indicates that this limit has been exceeded. The beginning of each experiment is indicated, with this restriction when necessary, and the end of each is also shown because, when a becomes small, the velocity tends to become independent of hydrogen-ion concentration, since the expression (1) approaches the form $k_5v/a = k_2l$ and all curves merge in the same "stem." When a is large, the increase in hydrogen-ion concentration, as reaction proceeds, may cause a rise in the curve as indicated by that for experiment Y. It should be emphasised that the branching is far outside the limits of experimental error, since in many cases the

first portion of the curve is very closely linear over a considerable range. The deduction to be drawn from these curves is that a part of the reaction velocity is contributed by an intermediate additive compound which is only formed slowly, taking some time to attain its maximum, and which is lacking at the beginning of an experiment. This also tends to account for another pronounced feature of several reactions, namely, as mentioned above, that reduction is very nearly a linear function of time throughout a large proportion of the total reaction; for instance, in experiment F no change can be detected in reaction velocity while the mercuric chloride decreases from 0·036 to 0·022, the other constituents being in relatively high

FIG. 1.

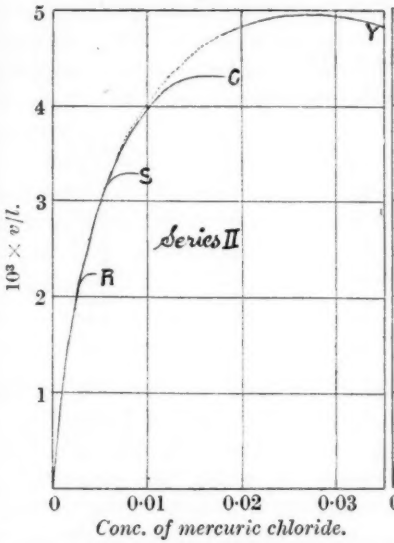
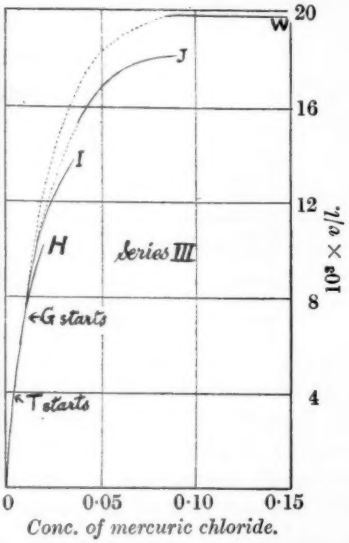


FIG. 2.



concentration. This linearity is doubtless the result of two opposing tendencies: the gradual accumulation of the intermediate compound tends to increase the velocity, while the reactions (I) and (II) tend to decrease only slowly—considerably more slowly than a decreases—owing to the form of expression (1).

The linear portion described above has to be neglected in calculating constants for these experiments according to the expression (4) (p. 1024) and the initial velocities are used separately to calculate other values in this expression. The difference between the two pairs of values thus calculated for a series is very slight in Series III (with $N/2{\cdot}2$-hydrochloric acid) where the linear portion and the branching are both slight, but is more distinct in Series II (with $N/11$-hydrochloric acid) where both the linear portions and the

branching are more pronounced. The difference between the experimental velocity at any stage of an experiment and the velocity calculated from the expression for the initial velocities of the corresponding series gives a measure of the formation of the intermediate compound. This is illustrated by experiment S in Table III; v_i is the velocity calculated from the initial velocities of the series as being equal to $10^{-6} \times 0{\cdot}0477hl/(1 + 0{\cdot}0577/a)$, and v_s, the "stem" velocity calculated from the expression $v_s \times 10^6 = 0{\cdot}046hl/(1 + 0{\cdot}038/a)$ as given by experiments V and Y (see Table IV), is also shown. It will be noticed that the experimentally-found velocity agrees with the stem velocity, within the limits of experimental error, after the stage at which the intermediate compound, as represented by the difference column, attains its maximum.

TABLE III.

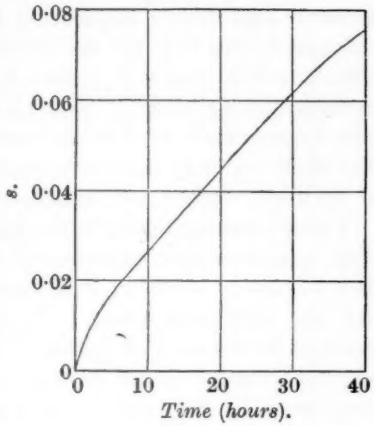
($hl = 0{\cdot}0108$ = constant).

a = $HgCl_2$.	$v \times 10^6$ (found).	$v_i \times 10^6$.	Diff. $\times 10^6$.	$v_s \times 10^6$ (calc.).
0·009	301	297	(−4)	331
0·008	300	281	19	318
0·007	297	264	33	301
0·006	283	243	40	275
0·005	261	219	42	259
0·004	233	191	42	230
0·003	195	157	38	195
0·002	146	116	30	148
0·001	87	65	22	87

An examination of the results of previous workers shows that the linearity would not be expected in the work of Linhart or of Garner, Foglesong, and Wilson, since they almost invariably restricted themselves to experiments in which the phosphorous acid was not greatly in excess, so that the ordinary curve, in which reduction of mercuric chloride is plotted against time, would not be linear; also, all but one of Linhart's experiments are in the presence of hydrochloric acid ranging in concentration up to $2N$, in which the main reactions (I) and (II) preponderate to such an extent as to obscure the subsidiary reactions. Curves plotted from Purkayostha and Dhar's work, however, give a definitely linear portion, since they used phosphorous acid in moderate excess, and those from the work of Montemartini and Egidi, in spite of erratic results, also give definite indications both of similar linear portions and of the large initial fall in velocity mentioned on p. 1017 as characterising experiments in which there is no extraneous chloride-ion. In the latter type of experiment the large initial fall is succeeded by a period in which the velocity is nearly constant until the last part of the reaction, when it again falls rapidly. For experiment B, which is

of the type under discussion, the initial concentrations of phosphorous acid and mercuric chloride were $M/11$ and $M/55$, respectively, and Fig. 3 represents the ordinary time–reduction curve, and Fig. 4 the v/l—a curve, that is, velocity per unit concentration of phosphorous acid plotted against mercuric chloride concentration.

FIG. 3.



Still another factor has to be considered and that is the effect of the chloride-ions on reactions in which they have reduced the reaction (IV) to negligible proportions. This consideration is deferred till the discussion of results.

A detailed examination of all the experimental results has shown that in most of the cases where one or more reactions are superimposed on the reactions (I) and (II), the contribution to be ascribed

FIG. 4.

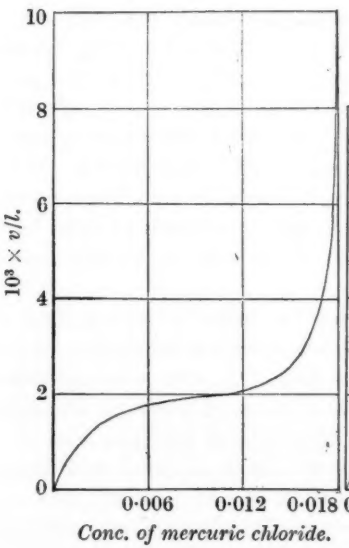
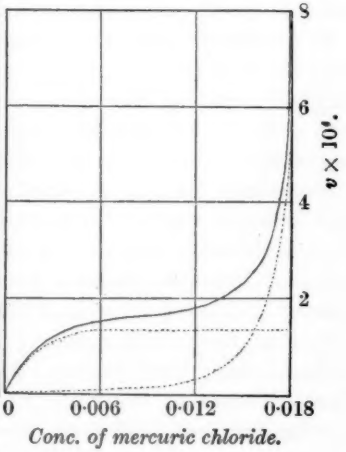


FIG. 5.



to the minor reactions is too greatly influenced by experimental error to be suitable for critical examination, since this contribution

has to be ascertained by the difference between the actual experimental velocity and that calculated as being due to the reactions (I) and (II). In the circumstances, all that it is possible to do is to find the value of k_5 which gives the most consistent value for k_2 in each experiment (neglecting linear portions for reasons already advanced) and to judge the influence of the minor reactions by their effect on the values of k_2 and k_5 thus obtained. These values are recorded in Table IV. Series I is omitted from this table because the experiments were in absence of initial extraneous chloride and the initial velocity falls off so rapidly that it is impossible to represent it with any approach to accuracy.

Unfortunately, owing to the form of the v/l—a curve (for example, Fig. 1), especially in experiments which have an initial linear portion, it is necessary to resort to integration to obtain the above constants for the following reason. In early attempts by the differential method to obtain the values of v, it was assumed that the velocity corresponding to a fall from a_1 to a_2 in mercuric chloride concentration may be ascribed to a concentration of $(a_1 + a_2)/2$, but an examination of the ordinary unimolecular expression shows that this process involves an error of 1 per cent. when 0·7—0·8 of the substance has been transformed, and of 4 per cent. when 0·8—0·9 has been transformed. In a bimolecular reaction the error attains a value of 1 per cent. half-way through the reaction and increases rapidly, reaching 11 per cent. over the range 0·8—0·9 of total reaction. It is therefore evident that the method is very inaccurate when the velocity changes relatively rapidly, and in the present reaction it is only when this is the case that the desired information can be obtained, since the linear portion of the velocity curve is useless for this purpose, as already noted. Integration affords a method of avoiding this error, which would have a large incidence on the velocity differential method, and it is justified here because examination of the curves has shown them to be of the type on which the integration formula is based.

The formula used for integration in order to find k_2 and k_5 is derived in the same way as that used in studying the reaction between iodine and hypophosphorous acid (*loc. cit.*), but a modification is necessary to allow for the fact that 2 mols. of mercuric chloride are involved in the stoicheiometric equation in the place of 1 mol. of iodine. Also, the constants have been designated with different suffixes in order to bring the notation of the reaction now under discussion into line with that between phosphorous acid and iodine. The assumptions involved are that there is a reversible change between the two forms of the acid, which is accelerated in both directions by hydrogen-ions, and that the second form only reacts

TABLE IV.

Series.	Expt.	a.	HCl.	NaCl.	HNO_3.	Mean h.	Mean c.	$10^6 \times v_0$.	$10^3 \times k_2$.	$10^3 \times k_3$.	Mean a.	$\frac{k_2}{(1-a)}$.	Mean f.
II	C	0·0182	0·0909	—	—	0·12	0·09	390	42—45	30—40	0·39	0·071	0·50
	R	0·0045	,,	—	—	,,	0·09	204	42	35	0·39	0·070	0·51
	S	0·0091	,,	—	—	,,	0·09	300	41	30	0·39	0·069	0·51
	V	0·0909	,,	—	—	,,	0·11	480	45—47	30—50	0·38	0·074	0·55
	Y	0·0364	,,	—	—	,,	0·12	425	47	38	0·37	0·074	0·50
III	G	0·0091	0·4545	—	—	0·41	0·40	630	52	47·5	0·25	0·069	0·18
	H	0·0182	,,	—	—	0·42	0·41	925	52	,,	,,	0·069	,,
	I	0·0364	,,	—	—	0·43	0·41	1260	53	,,	,,	0·071	,,
	J	0·0909	,,	—	—	0·44	0·42	1660	53·5	,,	,,	0·071	,,
	T	0·0045	,,	—	—	0·41	0·39	360	52	,,	,,	0·069	,,
	W	0·1591	,,	—	—	0·45	0·43	1810	53·5	,,	,,	0·071	,,
IV	E	0·0182	—	0·0909	—	0·05	0·09	150	36·5	40	0·52	0·075	0·53
	F	0·0364	—	,,	—	0·06	0·09	170	40	36—48	0·52	0·083	,,
	X	0·0909	—	,,	—	0·07	0·10	231	>50 *	—	0·48	>0·096	,,
V	U	0·0182	—	0·4545	—	0·05	0·34	127	33	40	0·51	0·067	0·20
	B′	0·0364	—	,,	—	0·06	0·35	139	(35)	40	0·51	(0·071)	0·21
	E′	0·0182	—	0·0091	—	0·05	0·02	175	48	46	0·51	0·098	0·86
	A′	0·0182	0·0455	—	—	0·09	0·05	269	42·5	36—44	0·445	0·075	0·65
	M	0·0182	0·1818	—	—	0·20	0·17	535	47	40	0·325	0·070	0·35
	O	0·0182	0·0909	—	0·0909	,,	0·09	600	43·5	(30)	0·325	0·065	0·51
	Q	0·0182	—	—	0·1818	,,	0·01	850	49	30	0·325	0·072	0·93
	L	0·0182	—	—	0·0909	0·12	0·01	545	(53)	(40)	0·39	(0·087)	0·95
	Z	0·0182	0·0455	—	0·0455	,,	0·05	390	44·5	31	0·39	0·071	0·66
	F′	0·0182	0·0909	0·3636	—	,,	0·36	335	41·5	42·5	0·39	0·068	0·20
	K	0·0182	—	—	0·4545	0·41	0·01	1175	53	28	0·25	0·070	0·93

* $k_2 = 50 \times 10^{-3}$ in $ds/dt = k_2hl$, the term involving k_3 being negligible over the range studied.

with mercuric chloride in such a way that the reaction is unimolecular with respect to the latter. Thus one has

$$(ds/dt)(1 + k_3h_t/k_4a_t) = k_2l_th_t \quad . \quad . \quad . \quad . \quad (2)$$

where the suffix t denotes concentration after time t, k_2 is the velocity coefficient of the direct change of the normal form of phosphorous acid to the second form, k_3 is that of the reverse change, and k_4 that of the reaction between the second form and mercuric chloride; the significance of a, l, h, and s has already been explained (p. 1015). Putting the ratio $k_3/k_4 = k_5$, and expressing (2) in terms of concentrations at zero-time, we have

$$(ds/dt)[1 + k_5(h + ms)/(a - 2s)] = k_2(l - s)(h + ms) \quad . \quad . \quad (3)$$

since the variation of h with s is nearly a linear function and m is a coefficient expressing this connexion. Integration gives

$$k_2t = [\log_e l/(l - s) + \log_e (h + ms)/h]/(h + ml) + k_5/(2l - a)\,[\log_e l/(l - s) - \log_e a/(a - 2s)] \quad . \quad . \quad (4)$$

In the discussion it is shown that k_2 is proportional to $(1 - \alpha)$, α being the degree of ionisation of phosphorous acid, thus showing that the molecule is concerned in the preliminary change (I); and also that, when the necessary allowance is introduced for the different conditions, this velocity coefficient agrees closely with that found for the same change underlying the reaction between phosphorous acid and iodine, thus showing the essential uniformity of the change.

Experimental.

The method chosen for following the reaction was to weigh the mercurous chloride produced; its solubility in water at 25° is approximately 0·0002 gram in 50 c.c., which was the volume usually employed, but in the strongest chloride concentrations it is 0·0008 gram, for which allowance is made. The method necessitates the use of a separate reaction-mixture for each determination, which tends to increase the experimental error, but duplicates show that the weights of mercurous chloride rarely differed by as much as a milligram in an average weight of 0·2 gram. For each experiment a stock of 500 or 1000 c.c. was made containing all the constituents required except the phosphorous acid, and portions of 50 c.c. (or occasionally 20 or 10 c.c.) were placed in wide test-tubes, the requisite volume (usually 5 c.c.) of a molar phosphorous acid solution being added at zero-time, both solutions being at 25°.

An unexpected difficulty was encountered in drying the filtered mercurous chloride. Linhart had dried his material slowly at 85°, in order to avoid loss with the water vapour, and finally at 105°.

In the author's experiments, it was desirable to localise experimental error by restricting each experiment to as few Gooch crucibles as possible, and more rapid drying was therefore necessary. The precipitate was washed with water and subsequently with a few c.c. of alcohol and ether successively and dried for 70 minutes at 95°. At 120° there was rapid loss, 3 mg. per hour, and at 110° about 0·6 mg. per hour, in spite of the fact that the vapour pressures of mercurous chloride at these temperatures are as low as 0·02 and 0·01 mm. respectively; at 95°, no further loss was ever noticed in half-an-hour's additional heating.

The methods of calculating the hydrogen-ion concentration are the same as those used in the reaction with iodine (*loc. cit.*), since Leblanc and Noyes (*Z. physikal. Chem.*, 1890, **6**, 329) have shown that the presence of mercuric chloride does not affect it.

In the concentrations in which it was employed, nitric acid was found to have no appreciable effect on either phosphorous acid or mercurous chloride.

Discussion of Results.

Certain of the results have already been discussed in the theoretical treatment. A more general survey will now be made of the results tabulated in Table IV, which shows for each experiment, other than some of Series I, the values obtained for k_2 and k_5, or, where the values are not very definite, the range of possible values; it also indicates the initial velocity, v_0, and the mean values during each experiment of the concentrations of hydrogen- and chloride-ions, of α, the degree of dissociation of the phosphorous acid, and of f, the average proportion of mercuric chloride which exists as such and is not combined in the complex ion $HgCl_3'$. All experiments given here started with the same concentration, 0·0911, of phosphorous acid, and the initial concentrations of mercuric chloride (a), and hydrochloric acid, nitric acid, or sodium chloride are shown.

Dealing first with Series III, the validity of the same two constants for the wide range covered by the whole course of each of the six experiments is noteworthy. It is illustrated by the use of the value 0·0475 for k_5 in two experiments (J and T) which represent widely different concentrations (Table V); and in experiment W, when readings are carried beyond the stage shown in Table II, all fourteen values of k_2 are between 0·0528 and 0·0542. The same two constants also express very closely the course of the only two comparable experiments in Linhart's work, namely, those in the presence of $N/2$-hydrochloric acid. It is of interest that, just as equation (1) tends to give a unimolecular form for the phosphorous acid when the

TABLE V.

(Experiment J).

$HgCl_2 = 0{\cdot}0909$, $H_3PO_3 = 0{\cdot}0911$, $HCl = 0{\cdot}4545$, $h_0 = 0{\cdot}41$, $m = 1{\cdot}64$, $k_5 = 0{\cdot}0475$.

t.	s.	$a-2s$.	$l-s$.	$k_2 \times 10^3$.
4·5	0·00722	0·0765	0·0839	54·1
6·1	0·00938	0·0721	0·0817	52·9
8·1	0·01243	0·0660	0·0787	54·0
8·65	0·01317	0·0646	0·0779	53·9
14·4	0·02015	0·0506	0·0708	53·0
18·9	0·02538	0·0391	0·0657	53·6
24·1	0·03032	0·0303	0·0608	53·6
30·0	0·03513	0·0206	0·0560	54·0
39·2	0·04011	0·0107	0·0510	53·8
				Mean 53·6

(Experiment T).

($HgCl_2 = 0{\cdot}004545$; other data as for J).

1·0	0·000324	0·00390	0·0908	(49·2) *
2·1	0·000665	$0{\cdot}00321_5$	0·0904	52·3
3·45	0·000998	0·00255	0·0901	52·0
4·8	0·001255	0·00203	0·0898	51·3
6·6	0·001545	0·00145	0·0896	51·9
8·65	0·001782	0·00098	0·0893	52·6
14·35	0·002095	$0{\cdot}00035_5$	0·0890	(50·8)
				Mean 52·0

* Based on 0·0084 gram Hg_2Cl_2.

mercuric chloride is in high concentration, as illustrated by experiment W, so it tends towards a unimolecular form for mercuric chloride when this is in very low concentration, owing to the fact that the second form of the acid is produced as rapidly as the mercuric chloride can utilise it; in agreement with this, all the determinations in experiment T give a unimolecular velocity coefficient for mercuric chloride which only deviates by 4 per cent. from the mean value until the reaction has exceeded 90 per cent. of the whole, at which stage the remaining mercuric chloride, being obtained by difference, is too largely influenced by experimental error to be known with sufficient accuracy.

For the majority of experiments in the table, it is seen that the value of k_2 is closely proportional to $(1 - \alpha)$ and the ratio $k_2/(1 - \alpha)$ is nearly constant at 0·070: this constancy is evidence in support of the hypothesis frequently advanced by the author in dealing with the reactions of hypophosphorous acid, that the reversible change between the two forms of the acid is due, not to the ion, but to the undissociated molecule. If it were due to the ion, k_2/α should be constant, but this is far from being so. The cause of the deviations from the above generalisation is examined later.

In dealing with the reaction between phosphorous acid and iodine, it was pointed out that k_2, which was obtained by methods ignoring

the hydrogen-ion concentration, was roughly proportional to this concentration. It is now seen that, when divided by the concentration, it is equal to $0{\cdot}073(1 - \alpha)$, as a mean, in four of the six series, the other two series being untrustworthy because of the large preponderance of another reaction which therefore introduces a large experimental error into the evaluation of k_2. There is thus but little doubt that in both these reactions of phosphorous acid the undissociated molecule is concerned, and the agreement between the values found for k_2 in the two reactions is cumulative (but not conclusive) evidence in favour of the assumptions involved.

Where reactions other than (I) and (II) are largely suppressed, there is good evidence that the function of the hydrogen-ion has been correctly interpreted—that it accelerates both the forward and the reverse attainment of equilibrium between the two forms of phosphorous acid.

The function of the chloride-ion has now to be considered. In the table it is seen that the chief deviations from the normal value of $k_2/(1 - \alpha)$ occur in experiments A′, E, E′, F, and X, since experiment L, having no initial extraneous chloride, is more appropriately considered with Series I. In the last one the high value of $k_2/(1 - \alpha)$ occurs with a high value of a coincident with a relatively low value of h : this divergence is attributable to reaction (V) (see p. 1018) by analogy with the iodine–phosphorous acid reaction. The first four of these experiments are characterised by low concentrations of either hydrogen- or chloride-ions or of both, so that the reaction which is suppressed by chloride-ions is still appreciable owing either to the low chloride concentration (for example, E′) or to the relative slowness of the other reaction which is accelerated by hydrogen-ions (for example, F). The phenomenon discussed with regard to Series I thus accounts qualitatively for these deviations and is applied quantitatively to experiment E′ on p. 1029, but, in the cases of experiments L and Q it is slight compared with the other reactions, which predominate in virtue of the high hydrogen-ion concentration, and in experiment K it is inappreciable for the same reason.

On the other hand, the active mass of the mercuric chloride is affected by the formation of complexes, so that even when reaction (IV) is quite suppressed the chloride-ions still have this other effect—compare experiments E and U, or F and B′. The column in Table IV which shows the proportion of mercuric chloride (f) which is not thus combined is calculated from the data of Sand (*Z. physikal. Chem.*, 1907, **59**, 424), who corrected the interpretation of Sherrill's results (*ibid.*, 1903, **43**, 705) and gave: $[HgCl_3'] = 11{\cdot}5 \times [HgCl_2][Cl']$. The values of k_5 are somewhat ill-definep because considerable

variations in the value often cause comparatively small changes in k_2; but, from experiments in which the value is well established, it may be concluded that low values for the proportion of free mercuric chloride correspond with high values for k_5, that is, if a in (4) is corrected to represent a diminished active mass for mercuric chloride, k_5 would have to be proportionally diminished. It is found that the correction of a to agree with *free* mercuric chloride introduces larger deviations in the opposite direction, from which it may be concluded that the complex is not inactive, but is nearly as active as the mercuric chloride to which it corresponds, and a similar conclusion is drawn from a consideration of Series I. This conclusion is, of course, subject to modification in the sense that the increase of chloride concentration may result in a negative "salt effect."

In order to investigate more closely the reaction which predominates in the early stages of experiments in Series I, the observed velocity has been reduced by that which may be calculated as due to reactions (I) and (II) from the expression $v_1 = 0{\cdot}070(1 - \alpha)hl/(1 + 0{\cdot}03h/a)$, since k_2 has been shown to approximate to $0{\cdot}070(1 - \alpha)$, and k_5 tends towards the value 0·030 when the chloride-ion concentration is low. The residual velocity thus found, v_2, is almost entirely due to reaction (IV), and the two component velocities are indicated by broken lines in Fig. 5 for experiment B as an example, one curve being nearly hyperbolic and the other of the form required by the combination of reactions (I) and (II), which is given by the expression for v_1. When v_2 is thus obtained as the difference between v and v_1 for the experiments of Series I, in which the initial concentration of phosphorous acid is uniformly 0·0911 and that of mercuric chloride ranges from 0·1818 to 0·0045, it is found that v_2 is approximately equal to $1{\cdot}8 \times 10^{-4}al/c_1$, where c_1 represents chloride-ions which are free and not involved in the complex ion $HgCl_3'$, as found from the data of Sand previously quoted. Using the data of Morse (*Z. physikal. Chem.*, 1902, **41**, 709), which were confirmed, as to order of magnitude, by Buttle and Hewitt (J., 1908, **93**, 1405), for the first stage dissociation of mercuric chloride $[HgCl^{\cdot}][Cl'] = 28 \times 10^{-8}[HgCl_2]$, we have $a/c = [HgCl^{\cdot}]/28 \times 10^{-8} = 35{\cdot}7 \times 10^5 \times [HgCl^{\cdot}]$, whence $v_2 = 640 \times l \times [HgCl^{\cdot}]$. The application of this idea is shown in Table VI, where experiment N is analysed in this way. It will be noted that the total mercuric chloride (a) is used and not that which is free; no constancy could be obtained by the use of the latter or by any assumption involving the concentration of hydrogen-ions. The deductions to be drawn from these facts are that the complex ion $HgCl_3'$ takes part in the reaction with the same order of rapidity as the free mercuric chloride, and, secondly, that hydrogen-

TABLE VI.

t.	$v \times 10^6$.	a.	c.	c_1.	$v_1 \times 10^6$.	$v_2 \times 10^6$.	l.	la/c_1.	$v_2c_1 \times 10^4/la$.
0	?	0·1818	0·0002	—	143	?	0·0911	—	—
0·5	?	0·1779	0·0037	0·0012	149	?	0·0892	—	—
1·0	1600	0·1760	0·0054	0·0018	152	1450	0·0882	8·60	1·68
1·5	1300	0·1746	0·0068	0·0023	155	1145	0·0875	6·65	1·72
2·0	1120	0·1734	0·0079	0·0027	156	965	0·0869	5·57	1·73
3·0	900	0·1714	0·0098	0·0034	160	740	0·0859	4·35	1·70
4·0	800	0·1698	0·0113	0·0040	162	640	0·0851	3·65	1·75
6·9	640	0·1659	0·0149	0·0054	167	475	0·0831	2·58	1·84
9·15	570	0·1631	0·0175	0·0064	171	400	0·0818	2·10	1·90
14·6	470	0·1574	0·0228	0·0086	178	290	0·0789	1·45	2·00
18·9	420	0·1536	0·0263	0·0102	182	240	0·0770	1·16	2·07
24·3	373	0·1493	0·0303	0·0122	186	190	0·0748	0·92	2·06
32·3	333	0·1429	0·0352	0·0146	192	140	0·0722	0·71	1·97
47·4	298	0·1340	0·0443	0·0198	200	98	0·0672	0·46	2·13
63·4	275	0·1247	0·0539	0·0257	205	70	0·0626	0·30	2·33

A difference of 2 units in the value 70×10^{-3} for $k_2/(1-a)$ causes a difference of 9 per cent. in the value of v_2 for the last determination, and, in the same determination, the experimental error of, say, 5 units in $v \times 10^6$ causes an error of 7 per cent. in v_2.

ions do not repress this reaction, so that it should be represented as (IV) rather than as

$$HgCl_2 + H_3PO_3 \text{ (normal form)} \rightleftharpoons X + H^{\cdot} + Cl' \quad . \quad . \quad (IVa)$$

(X being an intermediate complex formed by the equilibrium) which is an alternative interpretation of the facts described on p. 1018. A slight increase in the value of v_2c_1/al, as the reaction proceeds, could be explained by an equilibrium such as $HgCl_2 + H_3PO_3$ (normal form) $\rightleftharpoons (XH)^{\cdot} + Cl'$, but the additional arbitrary constant involved would make it more probable that the better agreement obtained is purely empirical. Similar alternative mechanisms were left undecided in the parallel reaction with iodine. The value of $1{\cdot}8 \times 10^{-4}$, which is mentioned above, is the mean of a great number which vary as much as from $1{\cdot}4 \times 10^{-4}$ to $2{\cdot}3 \times 10^{-4}$, but the method of deriving v_2 is extremely sensitive to experimental error, and, as a wide range of mercuric chloride concentrations is involved (0·004 to 0·182), the deviations are not regarded as unduly large. Moreover, experiment N, covering the widest variations in conditions, offers the most stringent test available, and the rapid change in velocity is liable to cause considerable errors in this differential method.

It is of interest to note that experiment E′, which was devised to test this hypothesis, has an initial velocity of 175×10^{-6}, whereas that due to reactions (I) and (II) is calculated as 129×10^{-6}, and v_2 is calculated as equal to 42×10^{-6}—a total of 171×10^{-6}.

Summary.

1. Former investigators have obtained widely divergent results owing to failure to detect the chief underlying reaction, namely, the reversible change of the normal form of phosphorous acid to another form which is responsible for a large proportion of the reaction, except in certain circumstances (see 5 and 6). Thus one has

$$H_3PO_3 \text{ (normal form)} \rightleftharpoons H_3PO_3 \text{ (second form)} \quad . \quad . \quad \text{(I)}$$

$$H_3PO_3 \text{ (second form)} + HgCl_2 + H_2O \longrightarrow H_3PO_4 + Hg + 2HCl \quad \text{(II)}$$

$$Hg + HgCl_2 \longrightarrow Hg_2Cl_2 \text{ (instantly)} \quad . \quad . \quad . \quad \text{(III)}$$

2. Their failure is due to the indiscriminate use of the process of integration.

3. The equilibrium (I) is accelerated in both directions by hydrogen-ions, and, as in the similar reaction of hypophosphorous acid, the undissociated molecule of the normal form is concerned.

4. The velocity coefficient for the forward change in this equilibrium is shown to be in substantial agreement with that deduced for the same change which has previously been found to underlie the reaction between phosphorous acid and iodine.

5. In the absence of extraneous chloride-ions initially, another reaction preponderates until the accumulation of chloride-ions reduces it to a lower order of magnitude :

$$HgCl^{\cdot} + H_3PO_3 \text{ (normal form)} + H_2O \longrightarrow H_3PO_4 + Hg + 2H^{\cdot} + Cl' \quad . \quad . \quad \text{(IV)}$$

6. In very low concentrations of hydrogen-ions (that is, in the presence of excess of sodium acetate) yet another reaction takes place which is almost instantaneous.

7. Evidence of still another reaction, involving the formation of an intermediate compound, is also advanced.

8. The effect of these reactions being superimposed, and also the effect of chloride-ions on the active mass of the mercuric chloride, are analysed qualitatively, but only reactions (I) and (II), and, to some extent (IV), are capable of quantitative demonstration.

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CXVII.—*The Activity of Hydrogen-ion in Aqueous Solutions of Hydrogen Fluoride.*

By WILLIAM FRANCIS KENRICK WYNNE-JONES and LAWSON JOHN HUDLESTON.

THE conductivity of hydrofluoric acid (Deussen, *Z. anorg. Chem.*, 1905, **44**, 312) shows it to be a typical weak electrolyte at concentrations less than $0{\cdot}02N$, for at dilutions greater than this the expression $\lambda_v^2/\lambda_\infty(\lambda_\infty - \lambda_v)V$ (I) is a constant, $7{\cdot}4 \times 10^{-4}$, presumably equal to the mass action constant $[H^\cdot][F']/[HF]$ (II). At greater concentrations the expression (I) increases rapidly with the content of hydrogen fluoride, and the acid resembles a transitional electrolyte. Pick (Nernst's "Festschrift," 1912, p. 360) assumed that the expression (II) remains constant and that the conductivity is affected by the formation of the complex ion HF_2'. From one conductivity measurement and an assumed mobility of the complex ion, he deduced a value for the mass action constant $[HF_2']/[HF][F']$ (III); further, on the assumption that no polymerisation to H_2F_2 occurs, he calculated, from his values for (II), (III), and the ionic mobilities, the conductivity for other concentrations and obtained good agreement with the experimental values. Davies and Hudleston (this vol., p. 260) studied the transference numbers and, by combining their data with those of Deussen for the conductivity, were able to reduce the assumptions to that of the constancy of (II), the nature of the complex ion, and the absence of appreciable polymerisation. The values so obtained for the concentrations of the undissociated molecules and the three ions, when substituted in (III), gave a fair constant for solutions up to $2N$.

If the expressions (II) and (III) are really constant, as assumed by these authors, the activities * of the individual ionic or molecular species must be proportional to their concentrations, and to test this point we have studied the E.M.F. of cells of the type $H_2|HF|KCl(sat.),HgCl|Hg$. This appears to be the first attempt to study an acid of intermediate strength such as hydrofluoric acid by this method, which had previously been applied only to strong acids such as hydrochloric acid or to very weak ones such as the organic acids.

EXPERIMENTAL.

Two saturated calomel electrodes were made and their constancy was tested against two identical, approximately semi-normal

* The term "activity" is here used in the sense defined by G. N. Lewis (Lewis and Randall, "Thermodynamics").

calomel electrodes. The fall of potential through the potentiometer wire was standardised by means of the usual cadmium cell. The materials for all these electrodes were prepared as follows. Mercury was passed one hundred times through a 45-mesh silk sieve into a metre tube containing 5 to 10 per cent. nitric acid. Further purification by electrolysis in nitric acid between platinum electrodes was found to be unnecessary. Mercurous chloride and sulphate were prepared electrolytically from this mercury by the method of Hulett (*Physical Rev.*, 1906, **23**, 166) and of Wolff and Waters (*Bureau Standards*, 1907, 70). A solution of "A.R." cadmium sulphate, saturated at 70°, was left in a shallow dish for one month to crystallise. From this, a 12 per cent. (by weight) amalgam was prepared by electrolysis. The potassium chloride was prepared by filtering a hot, nearly saturated, solution of a commercial sample through charcoal and fractionally crystallising four times. Solutions of hydrogen fluoride and sodium hydroxide were prepared by Davies and Hudleston's method (*loc. cit.*). The alkali was standardised against *N*/10-hydrochloric acid prepared by Hulett's distillation method (*J. Amer. Chem. Soc.*, 1909, **31**, 390). Ordinary distilled water was used throughout. For the preparation of the solutions of hydrogen chloride, hydrogen fluoride, and sodium hydroxide, it was freed from carbon dioxide by keeping it just below the boiling point while purified air was bubbled through it (Washburn's method).

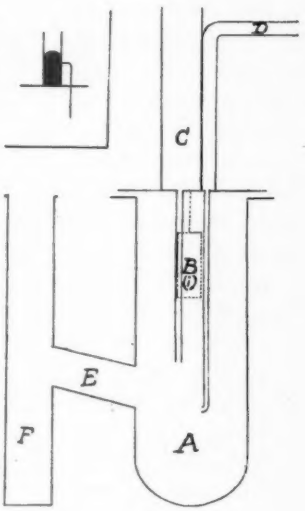
The standard cadmium cell, of the ordinary H-tube type, was tested against one bearing the National Physical Laboratory's certificate; the difference was at first nil and a month later barely 0·1 millivolt.

The calomel electrodes were of the form recommended by Lewis (*J. Amer. Chem. Soc.*, 1917, **39**, 2245), slightly simplified. They were carefully cleaned with chromic acid solution, washed with distilled water, and then the platinum leads were amalgamated by electrolysis of mercurous nitrate. After washing and filling, complete agreement was obtained in the *E.M.F.* given between either semi-normal electrode and one saturated electrode. The other unfortunately cracked and was rendered unfit for use.

The hydrogen electrodes consisted of strips of platinum foil, 1·5 × 0·5 cm., to which platinum leads were fused, mounted in a vessel of pure wax of the form shown in Fig. 1. *A* is a wax cylinder closed by a wax lid which bore two separate platinum electrodes (*B*) (only one shown), a funnel for introducing liquid (*C*), and an inlet tube (*D*) for the hydrogen, the last two being also of pure wax. The gas escaped through a pinhole in the lid. A branch tube (*E*) led to the side tube (*F*), and connexion between this and the other

electrolyte was made by means of an inverted U-tube of wax carrying at its highest point a side tube to which suction could be applied. Connexion with the platinum leads of the hydrogen electrodes was made as shown in the inset figure. This device was necessary, as in an earlier form of the apparatus great trouble was experienced owing to poisoning of the electrodes, believed to have been due to mercury reaching the surface of the platinum. In any case, the electrodes had to be replatinised daily. They were tested separately, and if the values differed by more than 0·0002 volt the experiment was rejected.

FIG. 1.



The *E.M.F.* was measured with a Pye's Student Potentiometer and a moving-coil galvanometer, readings being possible to 0·1 millivolt. The cells, etc., were immersed in a gas-heated water-thermostat at 25·00° ± 0·02°. The regulator was filled with benzene. Since the coefficients of expansion of benzene and toluene are 124×10^{-5} and 109×10^{-5}, respectively, and the specific heats 0·34 and 0·40, benzene would seem to be better suited for the purpose.

The concentration of the acid, measured in an "automatic" wax pipette, was determined by titration immediately before use. In all this work, the alkali was stored in wax vessels to prevent contamination with silica. A glass burette could be used for the titration as the time of contact with the alkali was not sufficiently long for perceptible quantities of silica to be dissolved. Phenolphthalein was used as indicator, and the fundamental standard, as already mentioned, was "Hulett" hydrochloric acid.

Hydrogen was taken from a cylinder, as previous experience had shown this to be of adequate purity. It passed first through a wash-bottle of pure wax containing the same acid solution as the cell. This also was immersed in the thermostat. All parts of the apparatus stood on metal supports connected together so as to act as an equipotential shield, as recommended by White (*J. Amer. Chem. Soc.*, 1914, **36**, 2011).

Hydrogen was passed through the cell and the wash-bottle, previously rinsed and filled, at the rate of one bubble per second for 2 or 3 hours. The accumulator was connected to the potentio-

meter ½ hour before making a reading and exact adjustment against the standard cell was made immediately before taking a reading. The liquid junction was then made and readings were taken at once with both hydrogen electrodes. The values invariably fell after a few minutes (see Fales and Vosburgh, *J. Amer. Chem. Soc.*, 1918, **40**, 1291). The calomel electrode was then checked against another chosen as standard, and the fall of potential across the potentiometer was checked once more against the standard cell.

Theory and Results.

When the cell H_2 | HF, | KCl(sat.),HgCl | Hg is generating current, the reaction which occurs is expressed by the equation $\frac{1}{2}H_2 + HgCl = HCl + Hg$. Adopting the notation of Lewis, we may write $E = E^0 - RT\log a_{HCl}a_{Hg}/a_{\frac{1}{2}H_2}a_{HgCl}$, where E^0 is the *E.M.F.* which would be given if all the substances were in their "standard" states, and a is the activity of the substance denoted by the suffix, under the conditions ruling when E is measured. The activities of the mercury and calomel remain at unity and that of the hydrogen, which occurs only to the one-half power, was so nearly so in our experiments as to make the correction for its variation only 0·2 or 0·3 millivolt (the total pressure varied between 750 and 770 mm. of mercury), so it was neglected. It is usual to assume that the reaction occurring at the electrodes can be split up into two parts, (*a*) $\frac{1}{2}H_2 = H^{\cdot} + e$ and (*b*) $HgCl + e = Hg + Cl'$ (where e denotes an electron), and to neglect any reaction taking place at the liquid junction. This amounts to neglecting the potential difference at the interface of the two liquids, a somewhat questionable proceeding even in the presence of saturated potassium chloride solution. In the absence of any known better method, however, this assumption will be made in the following argument.

Since $a_{HCl} = a_{H^{\cdot}} \times a_{Cl'}$, and the concentration (and therefore the activity) of the chlorine-ions round the electrode concerned remains constant, we may write $E = E' - RT\log a_{H^{\cdot}} = E' - 0{\cdot}0592\log a_{H^{\cdot}}$, E' being a constant. To obtain the numerical value of this, the cell was first filled with 0·1008*M*-hydrochloric acid, when E was found to be 0·3091 volt (which implies 0·3093 * volt for *M*/10-acid, for which G. N. Lewis gives the value $a_{\pm} = 0{\cdot}0814$, and this mean activity is presumably the same as that for each of the ions separately). With this value, we find $E' = 0{\cdot}2448$ volt.

The table shows the normality of the hydrofluoric acid (*N*),

* There is a zero correction of 0·3 millivolt to be added to this according to a table supplied by the manufacturer. This makes our value 0·3096, whilst Fales and Mudge (*J. Amer. Chem. Soc.*, 1920, **42**, 2434) found 0·3099 for the same combination. The value is uncorrected for pressure in each case.

the *E.M.F.* obtained against a saturated calomel electrode, and the calculated value of a_{H^+}. For comparison, the concentration deduced by Davies and Hudleston (interpolated graphically) is given in the fourth column, and the *E.M.F* calculated from this in the fifth.

TABLE I.

N.	*E* (found).	a_{H^+}.	[H$^+$].	*E* (calc.).
1·550	0·3040	0·1000	0·8800	0·3070
1·15	0·3100	0·0782	0·0668	0·3141
1·000	0·3120	0·0732	0·0588	0·3174 *
0·760	0·3200	0·0535	0·0460	0·3237
0·500	0·3320	0·0335	0·0319	0·3331
0·500	0·3315	0·0342	0·0319	0·3331 *
0·360	0·3420	0·0227	0·0240	0·3404
0·082	0·3650	0·0092	0·0085	0·3671
0·030	0·3820	0·0048	0·0048	0·3820

* These values were obtained with only one electrode functioning.

On plotting *E* or a_{H^+} against log *N* on a large scale, it will be seen that the two results agree within the limits of error for concentrations up to about 0·4*N*, after which the values of a_{H^+} are materially greater than those of [H$^+$]. This is unusual behaviour for an ion, and whether it is really so or whether there is an error arising from the potential at the liquid interface must remain for the moment an open question. Independent work on this point is in progress. It would seem, at any rate, to confirm the postulates of Davies and Hudleston in regard to solutions in which the concentration of the complex ion is considerably greater than that of the fluoridion.

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CXVIII.—*The Formation of Quaternary Ammonium Salts. Part II.*

By EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and WILLIAM CHARLES PECK.

p-BENZOQUINONE reacts with the pyridine salts of many organic acids (formic, acetic, propionic, benzoic, phenylacetic, phenylpropionic, cinnamic, benzenesulphonic, and naphthalene-β-sulphonic acids), as with those of inorganic acids (Barnett, Cook, and Driscoll, J., 1923, **123**, 503), with the formation of quinolpyridinium salts. Reaction takes place with difficulty and the products cannot be purified; they are, however, convertible into the picrate, which is readily obtainable.

The reaction which takes place when a compound containing an ethylenic bond is submitted to the simultaneous action of pyridine

and bromine, first examined by Ortoleva (*Gazzetta*, 1899, **29**, i, 503; 1903, **33**, ii, 51; *Atti R. Accad. Lincei*, 1903, [v], **16**, i, 874), has been investigated. Rarely has a definite product been isolated. Well-crystallised pyridinium salts have been obtained from anethole (I or II), *iso*safrole (III or IV), *cyclo*hexene (V), stilbene (VI), cinnamic acid (VII and VIII), and its methyl and ethyl esters (IX). Phenyl cinnamate, coumarin, 2 : 4- and 4 : 4′-dinitrostilbene, 2 : 4 : 3′-trinitrostilbene, anthraflavone, phenanthrene, and *as*.-phenyl-α-naphthylethylene were recovered unchanged, and terpineol, camphene, α-ionone, oleic acid, benzylideneacetone, and piperonylideneacetone underwent bromination. Quaternary salt formation probably occurred with eugenol, *iso*eugenol, safrole, ethylene, undecenoic acid, styrene, and with maleic, aconitic, itaconic, and citraconic acids, but pure products could not be isolated; in some cases unstable picrates were obtained. In the case of styrene, in addition to a very soluble quaternary salt, styrene dibromide was formed in about 35 per cent. yield. Since a sample of this was recovered unchanged after being kept in pyridine solution for 24 hours, it was not an intermediate stage in the formation of the quaternary salt, which must therefore have been due to a direct reaction of pyridine perbromide.

(I.) $MeO\cdot C_6H_4\cdot CH(NC_5H_5Br)\cdot CHBrMe$

II.) $MeO\cdot C_6H_4\cdot CHBr\cdot CHMe\cdot NC_5H_5Br$

(III.) $CH_2O_2{:}C_6H_3\cdot CH(NC_5H_5Br)\cdot CHBrMe$

$CH_2O_2{:}C_6H_3\cdot CHBr\cdot CHMe\cdot NC_5H_5Br$ (IV.)

$CH_2\cdot CH_2\cdot CHBr$
$CH_2\cdot CH_2\cdot CH\cdot NC_5H_5Br$ (V.)

(VI.) $CHPhBr\cdot CHPh\cdot NC_5H_5Br$

$CHPh(NC_5H_5Br)\cdot CHBr\cdot CO_2H$ (VII.)

C_5H_5N(PhCH·CHBr·CO)O (VIII.)

$CHPh(NC_5H_5Br)\cdot CHBr\cdot CO_2Me$(or Et) (IX.)

The substance obtained by Ortoleva (*loc. cit.*) by the action of pyridine and iodine on cinnamic acid, and also by James (J., 1913, **103**, 1368) by treating β-chloro-α-iodo-β-phenylpropionic acid with pyridine, is stable towards mineral acids, is insoluble in water, forms a periodide (James), and gives acetophenone on boiling with dilute sodium hydroxide solution. These properties are not in harmony with the constitution of pyridine α-iodocinnamate assigned to the substance by Ortoleva and James, but accord well with the betaine structure XI, formed by the reactions indicated:

$PhCHI\cdot CHI\cdot CO_2H \longrightarrow$ $PhCH(NC_5H_5I)\cdot CHI\cdot CO_2H$ (X.) $\longrightarrow$ C_5H_5N(PhCH·CHI·CO)O (XI.)

That it is the β- and not the α-iodine atom that reacts is clearly shown by James's synthesis of the compound. Evidence against Ortoleva and James's view is furnished by the facts that their compound cannot be formed from pyridine and α-iodocinnamic acid, and that α-iodocinnamic acid does not yield acetophenone on boiling with sodium hydroxide solution, even in presence of pyridine. The most definite proof of the betaine structure would be the preparation of a quaternary salt with a free carboxyl group (formula X) and its re-conversion into the betaine (XI). Owing to the instability of the compound, this has not been possible, and attempts to prepare a quaternary salt of the corresponding methyl and ethyl esters by treating the betaine with hydrogen chloride in alcoholic suspension were also unsuccessful, as no crystalline product could be isolated. With the corresponding bromine derivatives, however, there was no difficulty in obtaining direct proof of the betaine structure, as α-bromo-β-phenylpropionic acid-β-pyridinium bromide was isolated in the pure state and was found to pass easily into the betaine.

Experimental.

Dihydroxyphenylpyridinium Salts.—A solution of *p*-benzoquinone (1 gram-mol.) and the organic acid in slight excess in pyridine was heated on the water-bath for 2 hours. The highly coloured product was triturated with ether and recrystallised from water, alcohol, or a mixture of alcohol and ether. In the case of picric acid, the product was easily obtained pure and was identified by direct comparison with an authentic sample of dihydroxyphenylpyridinium picrate (Barnett, Cook, and Driscoll, *loc. cit.*). In the case of phenylacetic acid, brown leaflets, m. p. 160°, were readily obtained, although owing to the hygroscopic nature of the salt the analytical figures were not satisfactory (Found: C = 70·0; H = 5·26. $C_{19}H_{17}O_4N$ requires C = 70·6; H = 5·26 per cent.). In all cases, the partly purified product was dissolved in water, an aqueous solution of picric acid added, the resulting picrate purified by recrystallisation from water, and finally identified by direct comparison with an authentic sample.

vic.-*Bromopyridinium Salts.*

The following compounds were prepared by treating a well-cooled solution or suspension of the unsaturated compound in pyridine with bromine (1 mol.), also usually in pyridine solution. The product was collected after some time (15 minutes to 12 hours), washed with ether, and purified by recrystallisation.

β(or α)-*Bromodihydroanethole*-α(or β)-*pyridinium bromide* (I or II), twice recrystallised from a mixture of alcohol and ether and

twice from water, in which it is very easily soluble, forms a colourless, crystalline powder, m. p. 170—172° (decomp.) (Found: Br′ = 20·5. $C_{15}H_{17}ONBr_2$ requires Br′ = 20·7 per cent.). When it is boiled with a dilute solution of sodium hydroxide, a brown resin is precipitated and an odour of anethole produced.

β(or α)-*Bromodihydrosafrole*-α(or β)-*pyridinium bromide* (III or IV), recrystallised from water and from alcohol (Found: Br′ = 39·8. $C_{15}H_{15}O_2NBr_2$ requires Br = 39·9 per cent.), forms colourless needles, m. p. 193° (decomp.), which are sparingly soluble in cold water and cold alcohol. It is converted into a brown resin by boiling with dilute sodium hydroxide.

Under conditions similar to the above, safrole gave a product which could not be purified owing to its excessive solubility. It was probably a dipyridinium salt.

1-*Bromocyclohexane*-2-*pyridinium bromide* (V), recrystallised twice from a mixture of alcohol and ether (Found: Br′ = 24·9. $C_{11}H_{15}NBr_2$ requires Br′ = 24·9 per cent.), forms glistening, white needles which on heating sinter at 110° and melt at 165—170°. It is very easily soluble in water, and its aqueous solutions appear to remain unchanged when boiled with a dilute solution of sodium hydroxide.

The pyridine liquors from the above preparation when poured into dilute sulphuric acid yielded a heavy oil, which contained bromine but no nitrogen and agreed in its properties with 1 : 2-dibromo*cyclo*hexane.

β-*Bromo*-αβ-*diphenylethylpyridinium bromide* (VI), recrystallised from alcohol (Found: Br = 38·2. $C_{19}H_{17}NBr_2$ requires Br = 38·2 per cent.), forms glistening, white needles, m. p. 190—193°. It is very sparingly soluble even in boiling water and owing to partial decomposition (see below) cannot be conveniently purified by recrystallisation from this solvent. When boiled with a dilute solution of sodium hydroxide, it is converted into a brown resin which dissolves in organic solvents with an intense purple-red colour. During the production of this resin no smell of benzaldehyde can be detected.

β-*Hydroxy*-αβ-*diphenylethylpyridinium Bromide*.—Bromodiphenylethylpyridinium bromide (8·4 grams) and precipitated calcium carbonate (1 gram) were boiled with 750 c.c. of water until a clear solution was obtained (about half an hour). After concentrating to a small volume on the water-bath, the solution was cooled and the solid collected, dried in the steam-oven, and recrystallised from a mixture of alcohol and ether and from absolute alcohol (Found: Br = 22·6. $C_{19}H_{18}ONBr$ requires Br = 22·5 per cent.). This pyridinium salt forms small, colourless needles which sinter slightly

at 170° and melt to a clear liquid at 238—240°. It is easily soluble in hot water and hot alcohol, sparingly soluble in the cold. When its aqueous solutions are boiled with sodium carbonate, or more rapidly with sodium hydroxide, benzaldehyde (identified by the preparation of the phenylhydrazone) and a brown, resinous substance are produced.

α-Bromo-β-phenylpropionic acid-β-pyridinium Bromide (VII) *and Betaine* (VIII).—To a well-cooled solution of cinnamic acid (15 grams) in pyridine (30 c.c.), bromine (5 c.c.; 1 mol.) was slowly added. After keeping over-night, the almost solid mass was diluted with acetone and the solid (26 grams) collected and recrystallised from 20 per cent. hydrobromic acid (Found: Br′ = 20·8. $C_{14}H_{13}O_2NBr_2$ requires Br′ = 20·7 per cent.). This pyridinium bromide forms colourless crystals, m. p. 193—198° (decomp.). It is strongly acid in reaction and on boiling with water or alcohol loses hydrogen bromide and passes into the *betaine* (VIII). This forms a colourless, crystalline powder, m. p. 178—180°, which is almost insoluble in all the usual media (Found: Br = 26·2. $C_{14}H_{12}O_2NBr$ requires Br = 26·1 per cent.). When it is boiled with aqueous 2 per cent. sodium hydroxide, acetophenone (identified by the preparation of the semicarbazone) and a brown, resinous substance are formed. If it is kept for a day at the ordinary temperature, or if warmed on the water-bath for 1 minute, with 2 per cent. sodium hydroxide solution, α-bromocinnamic acid is formed, although the yield does not exceed 10 per cent.

Methyl and *ethyl α-bromo-β-phenylpropionate-β-pyridinium bromides* (IX) were recrystallised, the former from very dilute hydrobromic acid and then from alcohol (Found: Br′ = 20·0. $C_{15}H_{15}O_2NBr_2$ requires Br′ = 20·0 per cent.), and the latter from a mixture of alcohol and ether (Found: Br = 38·2. $C_{16}H_{17}O_2NBr_2$ requires Br = 38·5 per cent.). The methyl ester, glistening, white needles, and the ethyl ester have m. p. 178° (decomp.) and 157—158° (decomp.), respectively.

Both the above esters, if treated in hot aqueous solution with dilute 10 per cent. ammonia, lose the pyridinium group and pass into the methyl or ethyl ester of α-bromocinnamic acid. As the yields obtained are satisfactory (80—90 per cent.) and as the pyridinium salts are easily obtained, this method is a very convenient one for preparing methyl and ethyl α-bromocinnamates. If the hydrolysis of either pyridinium ester is effected by a cold alcoholic solution of potassium hydroxide (5—10 per cent.), both the pyridinium group and the alcohol radical are removed, the product in both cases being α-bromocinnamic acid. If the hydrolysis is brought about by boiling for 2 hours with alcoholic alkali, loss of

hydrogen bromide also takes place and phenylpropiolic acid is produced.

Attempts were made to extend the above reactions to phenyl cinnamate and coumarin. In neither case could any pyridinium salt be obtained, practically the whole of the original material being recovered unchanged.

In conclusion, the authors desire to express their thanks to Messrs. Burgoyne, Burbidges & Co., Ltd., for gifts of material, and to the Research Fund Committee of the Chemical Society for a grant which has defrayed part of the expense of this research.

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CXIX.—*The Correction of the Density of Liquids for the Buoyancy of Air.*

By GUY BARR.

DISCUSSING possible sources of error when density determinations of great accuracy are being made, Wade and Merriman (J., 1909, **95**, 2180) and Hartley and Barrett (J., 1911, **99**, 1073) give the formulæ

$$S_{t/t'} = D'' + \sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and $\delta_t = \delta_w \dfrac{W_3 - W_1 + \Delta_1(V_c - V_{pg})}{W_2 - W_1 + \Delta_1(V_c - V_{pg})}$, respectively (the symbols are defined in the papers). The former authors suggest the use of a solid glass counterpoise whose apparent weight is equal to that of the empty pyknometer. The maximum error indicated by them as being liable to be introduced by the approximations made in deriving equation (1), assuming all the errors mentioned to tend in the same direction, amounts to 1 in 100,000, more than half of this being due to neglecting the correction for buoyancy on the weights.* The possible variations in density of the air are assumed to be within the limits 0·00115 and 0·00125 gram/c.c.

Their equation may be written in the form

$$S_{t/t'} = \frac{W_3 - W_1 + \sigma_1 V}{W_2 - W_1 + \sigma_1 V} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where W_1, W_2, and W_3 are the weights (corrected for the air they displace) required to be added to the counterpoise when the pyknometer is weighed (1) empty, (2) filled with water at the temperature

* Actually the errors cannot be all at a maximum and in the same direction, and the greatest net error does not exceed 5 parts in a million.

$t°$, and (3) filled with the liquid at the same temperature, σ_1 is the density of the air at the time of finding the weight W_1, and V is the difference between the external volume of the counterpoise and the volume of the glass of the pyknometer.

Hartley and Barrett use as counterpoise a sealed bulb whose displacement is approximately equal to the volume of the liquid contained in the pyknometer when correctly filled. In comparing the procedures recommended by the two notes, it is seen that, although the equation (1) appears the more simple (chiefly in virtue of the substitution of D'' for the ratio of the weights, partly corrected, of liquid and water), it includes the term σ, which must be determined with the required accuracy each time the pyknometer is weighed full of liquid; any error in the observation of σ is transferred in full to the calculated density. In equation (2), on the other hand, σ does not appear, and in a series of measurements W_3 is the only fresh determination to be made for each filling: the values of W_1, V, and σ_1 may be observed with great care once for all; incidentally, an error in σ_1 amounting to 0·000006 gram/c.c. will occasion an error in $S'_{t°/t°}$ of less than 3 parts per million for specific gravities up to 2, whilst, as above indicated, a similar error in σ (equation 1) would cause a specific gravity approximately unity to be wrong by 6 parts per million. Formula (2) does in reality contain the densities σ_2 and σ of the air at the time of weighing the water and the liquid, since the apparent weights W_2 and W_3 are assumed to be corrected for air displaced by the brass weights. If W_1 is very small, as it will usually be, the correction on this will be negligible, and there will be no error greater than 6 in a million, between the extreme atmospheric conditions assumed, if, in these buoyancy corrections for the brass weights, either the density of air is supposed constant and equal to 0·00120 gram/c.c. or if, following Wade and Merriman, the apparent weight W_2 corrected with the appropriate value of σ_2, is increased by $W_2 \times 0{\cdot}00120/B$, where B is the density of the weights, and thereafter the apparent weight W'_3, uncorrected for air displaced, used in the equation in place of W_3.

Hartley and Barrett adopt Manley's hint (*Proc. Roy. Soc. Edin.*, 1900, **23**, 36) of making the counterpoise a little lighter than the empty pyknometer so that W_1 may be a positive quantity, and suggest that the condition—volume of counterpoise = volume of glass of pyknometer plus volume of liquid in pyknometer when adjusted to the mark—which must be satisfied in order to eliminate the densities σ_2 and σ of the air from the equations leading to formula (2), is sufficiently well met if the error in the adjustment amounts to 2 per cent.; with this error, the possible inaccuracy in the calculated

specific gravity may amount to 2 parts per million when S is about 1, or to 10 parts per million when S is about 2. There is little difficulty, with a pyknometer holding 25—50 c.c., in making the adjustment considerably closer. The final formula will obviously be much simplified if the further condition $W_1 = \sigma_1 V$ be satisfied exactly, for equation (2) then reduces to $S_{t/t} = W_3/W_2$. For this purpose, or for introduction into equation (2), the volume of the counterpoise and of the glass of the pyknometer will be most easily determined by finding the difference between their weights when weighed in air and in water. If a suitable solid rod is left when the counterpoise is sealed off after arranging V to be equal within, say, 1 per cent. to the content of the pyknometer, the subsequent fine adjustment of the weight by drawing off and grinding should not offer any difficulty. The air density σ_1 requires of course to be determined with the same accuracy as before, that is, it should be calculated from observations of pressure (read to 0·5 mm.), of temperature (known to within 0·2°), and of relative humidity: it will, in ordinary cases, cause only negligible errors if the air is considered to be half saturated.

In deriving formula (2) it has been tacitly assumed that the air inside the pyknometer when the weight W_1 is determined is of the same density as that in the balance case. But a Sprengel tube after being cleaned is usually dried by drawing dry air through it; if the capillaries are of small bore, it is probable that this dry air will remain inside during the weighing, in which case the equation requires to be modified by substituting $\sigma_d V_p$ for $\sigma_1 V$ in the numerator and denominator: V_p is the content of the pyknometer and σ_d is the density of *dry* air at the prevailing temperature and pressure. The use of dry air (for the density of which tables are more widely available) in the "empty" pyknometer has the practical advantage of reducing the weight of adsorbed moisture on the inner surface (see next paragraph); this surface is not, of course, reproduced in the counterpoise. When determining W_1 or making the final adjustment of the weight of the counterpoise, it is advisable to ensure that the density of the air in the pyknometer should be known, and since this necessitates drawing filtered air through the vessel, the use of dry air introduces no complication.

One of the arguments frequently adduced for the use of a glass counterpoise of surface similar to that of the pyknometer is that variations in weight due to differences in the amount of water adsorbed from air at varying humidities are thus compensated. Wade and Merriman state that the corrected weight of a glass pyknometer is practically constant; Manley (*loc. cit.*), on the other hand, cites observations which appear to demonstrate that variations

due to hygroscopicity are observable and are largely eliminated by the use of a counterpoise. From the *ad hoc* experiments of Warburg and Ihmori (*Wied. Ann.*, 1886, **27**, 481) it is evident, however, that even in the special case of a previously unused and poor glass the difference in weight of moisture adsorbed from atmospheres of relative humidity up to 90 per cent. does not amount to as much as 0·3 mg. per sq. dcm., and a short treatment with hot water reduces the variability to 0·03 mg. Weighings would practically never be made at so high a humidity, and the quantities of water adsorbed decrease rapidly as the humidity decreases. It is consequently improbable that the hygroscopicity of glass will normally occasion any appreciable error in density determinations, for a 50 c.c. pyknometer of conventional form has an external surface less than 1 sq. dcm. and the error due even to 0·3 mg. on this capacity is only 6 parts per million.

Changes in weight which may accumulate to a more considerable extent during a long series of measurements are those due to the action of the water of the thermostat on the glass, especially if the temperatures used are fairly high: for example, Mylius and Foerster (*Z. Instrumentenkunde*, 1891, **11**, 311) mention a flask which continually gave up alkali silicate equivalent to 0·05 mg. of Na_2O per hour to water at 80°. In so far as the exterior of the pyknometer is concerned, losses of weight due to such attack would be reproduced in a counterpoise of similar dimensions and of the same glass if it were always exposed to identical treatment.

If a resistant glass is employed in the construction of the pyknometer, the effects of hygroscopicity, and, for a reasonable period, of chemical attack may for most practical purposes be neglected, but the important advantage in the use of a sealed counterpoise, namely, that it obviates the necessity of any careful determination of air density at each filling of the instrument, should be sufficient to warrant its general adoption for precise routine work. Whilst the method in which a solid glass counterpoise is used allows the weight of the empty pyknometer to be checked as required without observations of air density, this is not the case when a sealed counterpoise is used as suggested. But although this check cannot be so readily applied, the more valuable because more comprehensive check of weighing full of water is most simply effected.

One source of error which appears to have been overlooked in the derivation of equations (1) and (2) is the assumption that the liquid filling the pyknometer displaces a volume of air which is fixed by the water calibration. This is obviously true only at the temperature at which the density is being determined, the volumes being adjusted to fill the apparatus to the mark at this temperature.

The majority of organic liquids have coefficients of expansion of the order of 0·001 per degree centigrade, whereas that of water is much less. Thus if, for example, the temperature of filling is 0° and the weighings are made at 25°, the water will have expanded by 0·003 c.c. and the organic liquid by 0·025 c.c. per c.c. These increases in the volume of air displaced necessitate corresponding increases in the expressions for the true weight of the material; for a liquid of density about 0·7 gram/c.c., the correction in the above circumstances would amount to 0·0012 (0·025/0·7 — 0·003) = 33 parts per million on the calculated specific gravity; for a liquid of density 2 gram/c.c., the correction would be reduced to 9 parts per million. For dilute aqueous solutions, the correction will nearly always be negligible: for organic liquids with high coefficients of expansion, the fifth decimal figure either of the density or of the specific gravity is not significant unless the temperature of filling is known to within 0·01°.

If the specific gravities experimentally determined and corrected as above are recorded as densities after multiplying by the density of the water used as standard of reference, it is, of course, important to recognise that modern tables of water densities are in gram/ml., not in gram/c.c.; the difference amounts to 27 parts per million. In view of this fact, the symbol $S_{t^\circ_4}$, which has its own definite meaning, should not be used to connote density.

In conclusion, two points may be mentioned which will occasionally be of some practical value in the construction of Perkin-Ostwald-Sprengel pyknometers. It is usual to make the capillary ends of the tube of uniform bore, and in order both to increase the precision of setting and to reduce the rate of evaporation, this bore is made small. Thus, if the volume is 50 c.c. and the adjustment to the fiducial mark may be in error by 0·2 mm., it is obvious that the diameter where this mark is made must not be more than 0·56 mm. if an accuracy of 1 part in a million parts is required. Through 3 cm. length of tubing of such a diameter, ether at 18° will evaporate at a rate of 1 mg. or more per hour, and the rate of loss is nearly proportional to the square of the diameter, but, especially when liquids of considerable viscosity are to be used, it is desirable to restrict the length of the capillary portion as much as possible so as to facilitate filling and cleaning; the bore may be as much as 2·5 mm. except near the ends.

The bulb which is provided in Perkin's modification of the pyknometer, to accommodate the expansion of the liquid when determinations at low temperatures are being made, should be as small as is consistent with the fulfilment of this requirement. For the volume which is not occupied by liquid at the temperature of weighing contains air, which may be assumed to be practically

saturated with the vapour of the liquid. If M is the molecular weight of the liquid and f its vapour pressure at the temperature considered in mm. of mercury, each c.c. of this air will weigh approximately $0{\cdot}0012f/760(M/28{\cdot}7 - 1)$ gram more than the ambient air; in the case of ether at 20° the increase amounts to 0·0011 gram per c.c. of unoccupied volume. Apart from errors due to actual escape of vapour from the pyknometer, which may be to some extent avoided by the use of caps or eliminated by observation of the rate of loss, the uncertainty as to the exact degree of saturation of the air above the liquid when the temperature is being varied makes the application of the correction suggested somewhat doubtful, so that the densities of very volatile liquids cannot be determined with high accuracy by the pyknometer method if it is necessary to allow for large expansions or contractions.

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CXX.—*The Application of Weerman's Reaction to a Methylated Sugar.*

By JAMES COLQUHOUN IRVINE and JOHN PRYDE.

ALTHOUGH the method of degrading sugars devised by Weerman (*Rec. trav. chim.*, 1917, **36**, 16; 1918, **37**, 16) depends on the capacity of an aldose to give an α-hydroxy-acid, we have applied the process to tetramethyl glucose in the expectation that a methyl group would be eliminated in the final reaction. In such an event, successive degradations would give a series of alkylated aldoses differing in the position of the internal oxygen ring, thus opening out a method of studying varied structural types of sugars.

Unfortunately, the investigation developed on unexpected lines and, so far, these possibilities have not been realised. Tetramethyl glucose was converted into tetramethyl gluconolactone, which reacted with ammonia to give tetramethyl gluconamide. This compound was normally transformed into the corresponding ammonium salt, but at temperatures of 100° and upwards ammonia was disengaged and tetramethyl gluconolactone regenerated. Moreover, the high dextrorotation of the amide is not consistent with the idea of a straight-chain structure and we prefer the constitution of an amino-lactone,

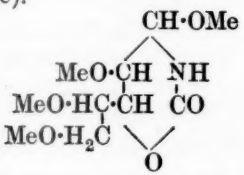
$$HO{\cdot}CH_2{\cdot}CH(OH){\cdot}\overset{\displaystyle\frown\!\!\!

This brings the compound into line with the hydrazino-lactones described by Blaise and Luttringer (*Compt. rend.*, 1905, **140**, 710), and with other amides studied by Fittig and Anschütz.

Although the conditions of the subsequent reaction between the amide and sodium hypochlorite were modified in numerous experiments, no carbon dioxide was evolved at any stage, and the product consisted entirely of the corresponding carbimide. On the analogy presented by a normal degradation, this carbimide should possess the straight-chain structure

$$MeO{\cdot}CH_2{\cdot}CH(OMe){\cdot}CH(OH){\cdot}CH(OMe){\cdot}CH(OMe){\cdot}N{:}C{:}O,$$

but the formula does not represent adequately the properties of the compound. Thus, it failed to undergo hydrolysis in the normal manner and displayed the notably high specific rotation of + 169°. Further, the nitrogen atom could not be expelled by the usual reagents and the properties are best expressed by the cyclic formula of the isomeric urethane (2-keto-4 : 5 : α : β-tetramethoxy-6-ethyl-tetrahydro-1 : 3-oxazine).



The optical activity of the urethane, dissolved in dilute hydrochloric acid, diminished to + 1·3° as the result of a complex reaction in which one methyl group was eliminated. The product showed feeble acidic properties, behaved as an unsaturated compound, and acquired an additional methyl group when heated with acid methyl alcohol. During this reaction, the rotation altered from dextro to lævo, but as no properties characteristic of a glucoside were developed, further exploration of the changes involved was not attempted. The essential result of the investigation is therefore the direct production, from a sugar, of derivatives in which nitrogen is present in a stable cyclic substituent. So far as can be ascertained, no transformation of this nature has hitherto been recorded.

Experimental.

Tetramethyl Gluconolactone.—This compound has already been prepared on a small scale by a somewhat different method (Purdie and Irvine, J., 1903, **83**, 1033). Sixty-five grams of bromine (4 atoms) were gradually added, with frequent shaking, to a solution of 50 grams of tetramethyl glucose (1 mol.) in 250 c.c. of water, and the mixture was shaken mechanically for 30 hours, after which the excess of bromine was removed at 40°/15 mm. On concen-

tration to half the volume, the liquid was shaken with litharge at 50° until the reaction was neutral to Congo-paper, filtered, and agitated with silver oxide until neutral to litmus. Insoluble silver salts were removed by filtration, and hydrogen sulphide was then passed through the solution to decompose silver tetramethyl gluconate, the liquid being thereafter filtered and concentrated under diminished pressure to a syrup. This was extracted with absolute alcohol, the solvent removed, and the residue taken up in anhydrous ether. After being filtered from traces of silver compounds, the solution was evaporated and the residual syrup distilled. Tetramethyl gluconolactone was thus obtained, in nearly quantitative yield, as a colourless, mobile liquid, b. p. 120—123°/0·5 mm., $n_D^{15°}$ 1·4580.

Tetramethyl Gluconamide.—Ammonia gas, after preliminary drying in the usual manner, was passed into anhydrous alcohol to saturation, after which the liquid was kept in contact with quicklime for several days. By gentle warming, the dried gas was disengaged and was led through lime towers into a 10 per cent. solution of tetramethyl gluconolactone in absolute alcohol. This procedure was successful in preventing the formation of ammonium tetramethyl gluconate, which is extremely difficult to remove. When saturation was complete, the solution was set aside for 12 hours and thereafter taken to dryness at the ordinary temperature in a vacuum desiccator. A viscous, neutral syrup, possessing a faint characteristic odour, was thus obtained and the mass gradually solidified in clusters of needles. Trouble was experienced in recrystallising the compound, but a mixture of high-boiling petroleum (3 parts) and ether (1 part) proved satisfactory. From this solution, the amide separated in fine, white needles which were difficult to manipulate owing to their soft, waxy nature and tendency to deliquescence, m. p. 68—70°, with preliminary softening; $[\alpha]_D^{15°}$ + 77·5° (in benzene, c = 1·224), + 60·4° (in acetone, c = 1·325) [Found: C = 47·71; H = 8·00; OMe = 47·1. Calc. for $C_6H_9O_2N(OMe)_4$, C = 47·81; H = 8·37; OMe = 49·4 per cent.]. As stated in the introduction, the properties of the compound indicate that it is an amino-lactone rather than a true acid amide.

Action of Sodium Hypochlorite on Tetramethyl Gluconamide.—This reaction was carried out on numerous occasions when the procedure was varied within wide limits, and the following account is restricted to conditions which gave a definite result. The hypochlorite was prepared according to Weerman's directions and the solution contained: available chlorine 5·57 and total alkali 9·87 per cent. This solution was used in the proportion of 150 c.c. to 1/10 gram-mol. of the amide. The latter was dissolved in water to

give a 20 per cent. solution, and to this the hypochlorite was slowly added with constant shaking. Towards the end of the reaction some nitrogen was evolved, but the evolution of gas was not vigorous and no spontaneous heating took place. After 10 minutes, when the reaction towards starch-iodide paper had become feeble, the solution was acidified with dilute hydrochloric acid and warmed, but no evolution of carbon dioxide was observed. After neutralisation with calcium carbonate, the solution was filtered, evaporated to dryness under diminished pressure, and the residue extracted with boiling absolute alcohol, the extract being evaporated again under diminished pressure. Treatment with boiling acetone separated the product from insoluble calcium salts, and the solution on concentration gave a crystalline residue mixed with a varying amount of syrup which consisted chiefly of tetramethyl gluconolactone. This was removed by boiling ether and the solid product purified by crystallisation from acetone. The compound possessed the composition of a tetramethyl gluconocarbimide, but the properties correspond with those of the isomeric urethane. Rectangular prisms, m. p. when heated rapidly 162°; when heated slowly, slight decomposition took place and the melting point was indefinite (150—160°) (Found: C = 48·07; H = 7·61; N = 5·73; OMe = 48·7. Calc. for $C_{10}H_{19}O_6N$, C = 48·19; H = 7·63; N = 5·62; OMe = 49·8 per cent.).

The compound was free from chlorine, was neutral in reaction, and showed $[\alpha]_D^{15°} + 169°$ for $c = 1·440$ in aqueous solution. No mutarotation was detected during a period of 24 hours.

Reactions of the Urethane.—When the compound was dissolved in 1 per cent. aqueous hydrochloric acid and preserved at 50°, the optical activity gradually diminished from $[\alpha]_D^{15°} + 161°$ to 1·3 in the course of 7 hours. The same change took place practically instantaneously when 4 per cent. acid was employed at 100°. The product of the change was isolated by neutralising with silver carbonate, this treatment giving a soluble silver salt which readily formed silver mirrors in the cold. After decomposition with hydrogen sulphide, followed by the customary procedure, the product was obtained as an amorphous solid. This behaved as an acid and had no effect upon Fehling's solution, but reacted readily with neutral potassium permanganate and with bromine. The composition corresponded with the formula $C_9H_{17}O_6N$ containing three methoxyl groups, so that one alkyl group had been lost in the reaction. The compound was accordingly heated for 5 hours at 120° with methyl alcohol containing 4 per cent. of hydrogen chloride, and the product isolated by the processes usually adopted in the case of an alkylated glucoside. A syrup was thus obtained

which on keeping crystallised partly in aggregates of fine needles. These, after spreading on porous porcelain, melted at 94—97°, and showed $[\alpha]_D^{15°}$ — 23·1° in acetone solution for $c = 1·148$. The methoxyl content had increased to OMe = 48·3 per cent., but the compound, which was not further examined, was not glucosidic and did not resemble a methylated arabinoside.

Acknowledgment is made to the Royal Commissioners for the 1851 Exhibition for a Research Scholarship which enabled one of us to take part in the investigation.

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CXXI.—*Mercuration of Nitrohydroxybenzaldehydes.*

By THOMAS ANDERSON HENRY and THOMAS MARVEL SHARP.

IN a previous paper (J., 1922, **121**, 1055) mercury compounds derived from the three hydroxybenzaldehydes were described and their constitution established * except as regards the acetoxymercuri-*m*-hydroxybenzaldehyde. It is now shown that the mercury in this substance must be in position 2, with respect to the aldehyde group, since on its replacement by the nitro-group there is formed the known 2-nitro-3-hydroxybenzaldehyde and similarly when the mercury residue is replaced by iodine, the iodo-*m*-hydroxybenzaldehyde produced is convertible, by heating with sodium hydroxide solution, into 2 : 3-dihydroxybenzoic acid.

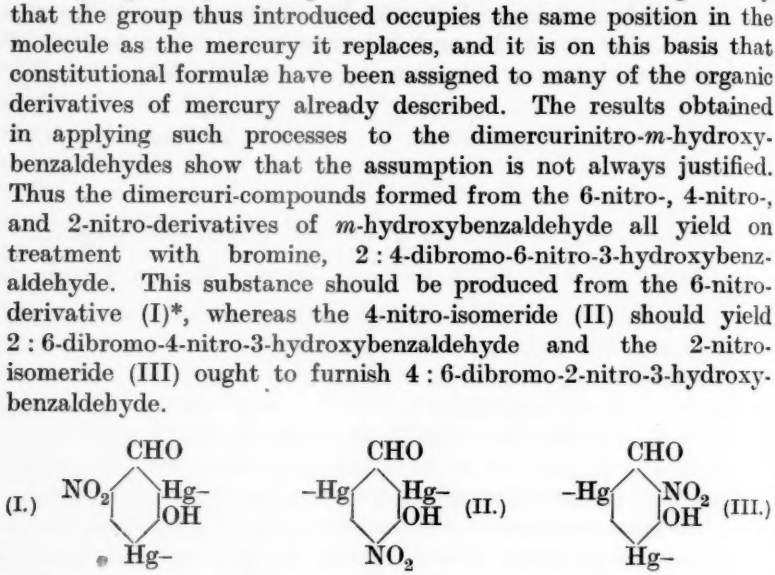
This work has now been extended to the nitro- and nitrohydroxybenzaldehydes. None of the three mononitrobenzaldehydes yields mercury derivatives even when boiled in solution with mercuric acetate for three weeks. The *m*-compound when boiled with mercuric acetate and sodium hydroxide is oxidised to *m*-hydroxybenzoic acid, m. p. 140—143° (corr.) [aniline salt, m. p. 115—116° (corr.)]. The nitrohydroxybenzaldehydes † on the contrary are readily mercurated. 3-Nitro-4-hydroxybenzaldehyde when boiled in 50 per cent. alcoholic solution with one molecular proportion of mercuric acetate yields only 5-hydroxymercuri-3-nitro-4-hydroxybenzaldehyde. The three known mononitro-3-hydroxybenzaldehydes each yield both mono- and di-mercuri-derivatives, which

* The melting point of 3 : 5-diacetoxydimercurisalicylaldehyde by a clerical error was given as 133° (decomp.) instead of 233° (decomp.; corr.) in the previous paper.

† The mercuration of nitro-*o*-hydroxybenzaldehydes has already been investigated by Whitmore and Middleton (*J. Amer. Chem. Soc.*, 1923, **45**, 1330).

can be separated by fractional crystallisation from appropriate fatty acids; if the mercuric acetate is increased to two molecular proportions the product consists almost entirely in each case of the corresponding dimercuri-derivative, very little of the mono-compound being formed.

In such compounds, the mercury can usually be replaced by a nitro-group or by a halogen, and it has been assumed generally that the group thus introduced occupies the same position in the molecule as the mercury it replaces, and it is on this basis that constitutional formulæ have been assigned to many of the organic derivatives of mercury already described. The results obtained in applying such processes to the dimercurinitro-*m*-hydroxybenzaldehydes show that the assumption is not always justified. Thus the dimercuri-compounds formed from the 6-nitro-, 4-nitro-, and 2-nitro-derivatives of *m*-hydroxybenzaldehyde all yield on treatment with bromine, 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde. This substance should be produced from the 6-nitro-derivative (I)*, whereas the 4-nitro-isomeride (II) should yield 2 : 6-dibromo-4-nitro-3-hydroxybenzaldehyde and the 2-nitro-isomeride (III) ought to furnish 4 : 6-dibromo-2-nitro-3-hydroxybenzaldehyde.



The steps taken to ensure the purity and identity of the initial materials, proof that the three dimercuri-compounds are different, and evidence of the identity and constitution of the single dibromo-nitro-*m*-hydroxybenzaldehyde yielded by the three are detailed in the experimental portion and need not be summarised here. The authors are of opinion that the data given leave no room for doubt that in the action of bromine on the two dimercuri-compounds formed from the 2-nitro- and 4-nitro-*m*-hydroxybenzaldehydes each nitro-group changes position with the bromine atom, which replaces the mercury atom in position 6.

This anomalous behaviour with bromine made it difficult to determine the position of the mercury residues in the 4-nitro- and 2-nitro-derivatives and it has not been found possible to replace mercury in these substances by nitro-groups. Fortunately, they behave normally with iodine and with the assistance of the results

* In these formulæ, Hg– represents a mercuri-residue –HgOH, –HgOAc, etc.

of this reaction it has been possible to suggest the three formulæ already given for these products.

The monomercuri-derivatives of all three nitro-compounds have been obtained, but only in small amounts and although each yields, on replacement of the mercury by iodine, a characteristic iodo-compound, none of these is known and the quantities obtainable so far have precluded the determination of the position of the iodine, and therefore also of the mercury in the original compounds, although it is probable that the mercury residue is in each case ortho- to the hydroxyl group.

As in the case of the mercurated hydroxybenzaldehydes described in the previous paper, the bactericidal action of these new compounds has been determined by Major Brown, C.I.E., M.B., B.Ch., of the Wellcome Bureau of Scientific Research, who finds that *Bacillus typhosus* is killed in 5 minutes by solutions containing (*a*) 0·004 per cent. of chloromercuri-4-nitro-3-hydroxybenzaldehyde, (*b*) 0·06 per cent. of either the 2 : 4-dihydroxydimercuri-6-nitro- or 4 : 6-dihydroxydimercuri-2-nitro-derivative of *m*-hydroxybenzaldehyde, (*c*) by amounts intermediate to these of the other mercury derivatives of *m*-hydroxybenzaldehyde, or (*d*) 0·12 per cent. of the 5-hydroxymercuri-3-nitro-derivative of *p*-hydroxybenzaldehyde. For these bactericidal trials, the compounds were used in the form of potassium salts.

Experimental.

2-*Acetoxymercuri*-3-*hydroxybenzaldehyde*,

$$CH_3{\cdot}CO{\cdot}O{\cdot}Hg{\cdot}C_6H_3(OH){\cdot}CHO$$

(J., 1922, **121**, 1059).—When a molecular mixture of this substance with potassium nitrate is added to sulphuric acid cooled below 0°, a small yield of 2-nitro-3-hydroxybenzaldehyde is obtained, identical, as shown by determination of the mixed melting point, with that prepared by Friedländer and Schenck's method (*Ber.*, 1914, **47**, 3043).

The iodo-3-hydroxybenzaldehyde obtained from the same mercury compound by the action of iodine in potassium iodide (*loc. cit.*), when heated at 100° with a 50 per cent. aqueous solution of sodium hydroxide, furnishes a small yield (accompanied by much dark brown acid resin) of an acid melting at 203°, which gives an insoluble lead salt, a blue colour with ferric chloride, changing to red on addition of sodium bicarbonate, and when mixed with recently ignited ground pumice stone and heated yields a crystalline sublimate having the characters of catechol (m. p. 103—104°, green colour with ferric chloride). The 2 : 3- and 3 : 4-dihydroxybenzoic acids are the only acids likely to yield catechol in this way, and of

these the 3 : 4-dihydroxybenzoic acid (protocatechuic acid) depresses the melting point of the acid under discussion to 166°. All the reactions of the latter acid are characteristic of 2 : 3-dihydroxybenzoic acid, and the authors have no doubt they are identical, although combustions of their acid did not give good results (Found : C = 55·6, 55·9; H = 4·12, 4·12. Calc., C = 54·5; H = 3·9 per cent.) owing to the difficulty of removing the last traces of the accompanying brown resin from the small total quantity of acid obtained. This iodo-*m*-hydroxybenzaldehyde undergoes decomposition with remarkable ease, and of the reactions tried with a view to its identification only the above has given a useful product, and that in a yield less than 2 per cent. of the theoretical.

In view of the production from it, as just described, of 2-nitro-3-hydroxybenzaldehyde and 2 : 3-dihydroxybenzoic acid, the original mercury compound must be 2-acetoxymercuri-3-hydroxybenzaldehyde.

Mercuration of Nitrohydroxybenzaldehydes.

The mercuration was effected in the same way throughout, namely, by boiling under reflux the nitrohydroxybenzaldehyde (1 mol.) with mercuric acetate (1 mol. or 2 mols.) in 50 per cent. alcohol containing a little acetic acid, boiling being continued until the mixture dissolved completely on adding sodium hydroxide solution.

The 3-nitro-4-hydroxybenzaldehyde used was prepared by Paal's method (*Ber.*, 1895, **28**, 2415); the yield obtained was 70 per cent. of the 4-hydroxybenzaldehyde used and the melting point was, as recorded, 141—142°.

5-*Hydroxymercuri*-3-*nitro*-4-*hydroxybenzaldehyde*, $HO{\cdot}Hg{\cdot}C_6H_3(OH)(NO_2){\cdot}CHO$.—This substance, obtained in quantitative yield by the general method, separates from the boiling solution in microscopic, orange platelets, which darken at about 285°, but do not melt at 300°. It is purified by solution in sodium hydroxide, in which it dissolves to form a deep orange-red liquid, and precipitation with carbon dioxide (Found : Hg = 52·46; N = 3·76. $C_7H_5O_5NHg$ requires Hg = 52·29; N = 3·65 per cent.). Addition of dilute hydrochloric acid to such a solution causes the precipitation of 5-*chloromercuri*-3-*nitro*-4-*hydroxybenzaldehyde*, which crystallises from alcohol in tufts of minute, colourless needles, m. p. 226° (decomp.; corr.) (Found : Hg = 49·77. $C_7H_4O_4NClHg$ requires Hg = 49·89 per cent.). The hydroxymercuri-compound is insoluble in the usual solvents except glacial acetic acid, from which there slowly separate colourless prisms of 5-*acetoxymercuri*-3-*nitro*-4-*hydroxy*-

benzaldehyde (Found : Hg = 47·15. $C_9H_7O_6NHg$ requires Hg = 47·13 per cent.). This darkens on heating at about 250°, but does not melt at 300°.

On shaking the finely powdered hydroxymercuri-compound with excess of a 5 per cent. solution of iodine in potassium iodide, the mercury is removed as mercuric iodide and a quantitative yield of the sparingly soluble (in potassium iodide) potassium salt of an *iodo-3-nitro-4-hydroxybenzaldehyde* is obtained. The free phenol crystallises from chloroform in yellow plates, m. p. 171—172° (corr.) (Found : C = 28·82, 28·30; H = 1·58, 1·97; N = 4·64; I = 43·38. $C_7H_4O_4NI$ requires C = 28·68; H = 1·37; N = 4·78; I = 43·33 per cent.). On oxidation with alkaline permanganate it is converted into 5-iodo-3-nitro-4-hydroxybenzoic acid, m. p. 247° (decomp.; corr.) (Found : I = 41·02. Calc., I = 41·08 per cent.), alone or mixed with a specimen prepared by Gerland's method (*Annalen*, 1854, **91**, 192). Kharasch (*J. Amer. Chem. Soc.*, 1921, **43**, 1204) gives the melting point as 251°.

The mercury compound formed from 3-nitro-4-hydroxybenzaldehyde must therefore be 5-hydroxymercuri-3-nitro-4-hydroxybenzaldehyde.

6-Nitro-3-hydroxybenzaldehyde was obtained, along with 4-nitro-3-hydroxybenzaldehyde and 2-nitro-3-hydroxybenzaldehyde, by nitrating *m*-hydroxybenzaldehyde according to Pschorr's process (*Ber.*, 1901, **34**, 4400) and separating the isomerides by Friedländer and Schenck's method (*loc. cit.*). When crystallised from benzene, they have the following characteristics, the figures in parenthesis being the melting points recorded by Friedländer and Schenck :— 6-Nitro-3-hydroxybenzaldehyde, long, thin, yellow needles, m. p. 170—171° (166°); 4-nitro-3-hydroxybenzaldehyde, thick, four-sided, yellow plates, m. p. 134° (128°); 2-nitro-3-hydroxybenzaldehyde, small, colourless prisms, m. p. 157° (152°). These characteristic forms invariably separate from any mixture crystallised slowly from benzene.

When molecular proportions of 6-nitro-3-hydroxybenzaldehyde and mercuric acetate are treated by the general method, an orange-coloured solid (A), which consists wholly of dimercurated products, separates from the boiling solution and is filtered off hot at the end of the reaction. On cooling and concentrating the filtrate, further amounts of solid, lighter in colour and consisting of mixtures of mono- and di-mercurated products along with unchanged 6-nitro-3-hydroxybenzaldehyde, are obtained.

The solid (A) appears to be a mixture of diacetoxydimercuri- and dihydroxydimercuri-compounds (Found : Hg = 64·12; N = 2·24. $C_{11}H_9O_8NHg_2$ requires Hg = 58·62; N = 2·05. $C_7H_5O_6NHg_2$

requires Hg = 66·83; N = 2·33 per cent.). It is insoluble in the usual organic solvents, but dissolves in formic, acetic, propionic, or *n*-butyric acid, and is best purified by solution in propionic acid, from which it separates as orange-yellow needles of 2 : 4-*dipropionoxydimercuri*-6-*nitro*-3-*hydroxybenzaldehyde* (the propionoxymercuri-group = $-HgO{\cdot}CO{\cdot}C_2H_5$) (Found: Hg = 56·26. $C_{13}H_{13}O_8NHg_2$ requires Hg = 56·32 per cent.) exploding at 235° (corr.). This substance is sparingly soluble in sodium hydroxide solution to an orange-coloured liquid (the solid itself is coloured bright red by alkalis) which is decomposed by hydrochloric acid with precipitation of 2 : 4-*dichlorodimercuri*-6-*nitro*-3-*hydroxybenzaldehyde*; the latter crystallises from alcohol in colourless, microscopic needles (Found: Hg = 57·97; N = 2·14; Cl = 10·56. $C_7H_3O_4NCl_2Hg_2 + 3H_2O$ requires Hg = 58·03; N = 2·03; Cl = 10·26 per cent.).

The monomercurated compound is obtained from the more soluble fractions of the mixture by extracting the finely ground substance with ether to remove unmercurated material, dissolving the residue in potassium hydroxide solution, and precipitating with hydrochloric acid. The pale yellow solid thus obtained is crystallised from alcohol, whence *monochloromercuri*-6-*nitro*-3-*hydroxybenzaldehyde* is easily obtained (Found: Hg = 49·98. $C_7H_4O_4NClHg$ requires Hg = 49·89 per cent.). It decomposes at 198° (corr.).

The dimercurated compound on agitation with a cooled, freshly prepared 5 per cent. solution of bromine in alcohol gives a clear liquid, which after concentration to remove most of the alcohol yields when poured into water a white precipitate; this, after drying and crystallising from chloroform, furnishes colourless prisms, m. p. 152·5° (decomp.; corr.) (Found: Br = 49·14; C = 26·18; H = 1·19. $C_7H_3O_4NBr_2$ requires Br = 49·20; C = 25·86; H = 0·92 per cent.). Yield 96 per cent. This is proved to be 2 : 4-*dibromo*-6-*nitro*-3-*hydroxybenzaldehyde* by the following reactions. On oxidation with alkaline permanganate, it is converted into an acid crystallising from water in colourless, soft needles, m. p. 230° (decomp.; corr.) (Found: Br = 47·43. $C_7H_3O_5NBr_2$ requires Br = 46·89 per cent.). 2 : 4-Dibromo-6-nitro-*m*-cresol, on oxidation with alkaline permanganate, yields 2 : 4-*dibromo*-6-*nitro*-3-*hydroxybenzoic acid* in 10 per cent. yield along with much unoxidised material, which is identical with the acid obtained from the mercury compound. The latter must therefore have the mercury residues in positions 2 and 4.

Shaking the dimercurated compound with a 5 per cent. solution of iodine in potassium iodide causes the mercury to be replaced

by iodine with the formation of 2 : 4-*di-iodo*-6-*nitro*-3-*hydroxybenzaldehyde* in almost quantitative yield. This substance crystallises from alcohol in hard, yellow prisms or thick needles, m. p. 142° (decomp.; corr.) which darken on keeping and lose their transparency (Found : I = 61·08. $C_7H_3O_4NI_2$ requires I = 60·60 per cent.). The *semicarbazone* melts at 214° (decomp.; corr.) and the *oxime* at 207—208° (decomp.; corr.). In addition, there is sometimes formed a compound which melts at 184° (decomp.; corr.), but the precise conditions for its production have not been determined. It is a *mercuric iodide additive compound* of 2 : 4-di-iodo-6-nitro-3-hydroxybenzaldehyde and can also be obtained by mixing the di-iodo-compound (2 mols.) with mercuric iodide (1 mol.) and crystallising the mixture from alcohol, when it separates in soft, yellow needles which darken on keeping (Found : Hg = 16·2. $2C_7H_3O_4NI_2,HgI_2$ requires Hg = 15·5 per cent.). Mercuric oxide is not precipitated from this compound by sodium hydroxide solution, but hydrogen sulphide decomposes it, forming mercuric sulphide and 2 : 4-di-iodo-6-nitro-3-hydroxybenzaldehyde.

On shaking the crude mono-mercury compound with excess of iodine solution, there is obtained a *mono-iodo*-6-*nitro*-3-*hydroxybenzaldehyde*, crystallising from alcohol in short, shining, yellow prisms, m. p. 206° (decomp.; corr.) (Found : I = 44·00. $C_7H_4O_4NI$ requires I = 43·33 per cent.). This mono-iodo-compound also loses its transparency on keeping and after several months becomes almost black in colour. There is also formed a small amount of the di-iodo-compound melting at 142° (decomp.).

When two molecular proportions of mercuric acetate are used for the mercuration, the product consists almost entirely of dimercurated compounds, but the last crops contain a little monomercurated substance, which is difficult to separate, but is proved to be present by the formation of the mono-iodo-compound melting at 206° on treatment with iodine.

4-Nitro-3-hydroxybenzaldehyde, treated by the general method described above, yields an orange-coloured solid consisting wholly of dimercurated compounds, which is filtered off hot. On cooling the filtrate, a mixture of mono- and di-mercurated products separates and on concentration the mother-liquors yield mainly a monomercurated product, mixed with unchanged 4-nitro-3-hydroxybenzaldehyde and a little of the dimercurated compound.

The dimercurated substance from its analysis appears to be a *hydroxymercuri-acetoxymercuri*-4-*nitro*-3-*hydroxybenzaldehyde* (Found : Hg = 62·38. $C_9H_7O_7NHg_2$ requires Hg = 62·47 per cent.). It is insoluble in most organic solvents, but dissolves in hot formic acid, from which, on cooling, pale yellow needles of

2 : 6-*diformoxydimercuri*-4-*nitro*-3-*hydroxybenzaldehyde* (the formoxymercuri-group = — Hg·O·COH) (Found : Hg = 61·62. $C_9H_5O_8NHg_2$ requires Hg = 61·13 per cent.) crystallise out. On heating, this substance darkens at 120° and explodes at 257°, but does not melt. Boiling with formic acid decomposes it with separation of metallic mercury. The compound is soluble in potassium hydroxide to a deep red solution, from which hydrochloric acid precipitates 2 : 6-*dichlorodimercuri*-4-*nitro*-3-*hydroxybenzaldehyde*. The latter crystallises from alcohol in bundles of minute, pale yellow needles, which darken on heating at 240°, but do not melt at 300° (Found : Hg = 61·32. $C_7H_3O_4NCl_2Hg_2,H_2O$ requires Hg = 61·24 per cent.). The compound loses a molecule of water at 60° in a vacuum and the anhydrous substance decomposes at 282° (corr.). The solution in potassium hydroxide is decomposed by carbon dioxide with precipitation of 2 : 3-*anhydro*-2 : 6-*dihydroxydimercuri*-4-*nitro*-3-*hydroxybenzaldehyde* (Found : Hg = 68·73. $C_7H_3O_5NHg_2$ requires Hg = 68·92 per cent.).

The mixture of mono- and di-mercurated compounds can be separated into its components by repeated extraction with cold formic acid, in which the mono-compound is the more soluble, precipitation of the mercury compound by addition of ether, and finally crystallisation of each fraction from formic acid (Found : for the mono-compound, Hg = 49·00. $C_8H_5O_6NHg$ requires Hg = 48·74 per cent. Found : for the di-compound, Hg = 61·63. $C_9H_5O_8NHg_2$ requires Hg = 61·13 per cent.).

Monoformoxymercuri-4-*nitro*-3-*hydroxybenzaldehyde* melts at 233—235° (decomp.; corr.). The mixture containing only a little dimercurated compound is best purified by steam distillation to remove 4-nitro-3-hydroxybenzaldehyde, and crystallisation of the residual mercury compound from propionic acid. Pale orange needles of *propionoxymercuri*-4-*nitro*-3-*hydroxybenzaldehyde* are thus obtained (Found : Hg = 45·07. $C_{10}H_9O_6NHg$ requires Hg = 45·62 per cent.). The solution of this in potassium hydroxide gives on addition of hydrochloric acid a yellow precipitate of *chloromercuri*-4-*nitro*-3-*hydroxybenzaldehyde*, which decomposes on heating at about 187° (Found : Hg = 50·23. $C_7H_4O_4NClHg$ requires Hg = 49·89 per cent.). The same products are obtained (the dimercurated compound in predominating amount) when two molecular proportions of mercuric acetate are used for the preparation.

On shaking the dimercurated compound with excess of a freshly prepared, cooled 5 per cent. solution of bromine in alcohol, there is formed in 80 per cent. yield a dibromo-compound, which crystallises from chloroform in colourless prisms, m. p. 152·5° (decomp.; corr.) (Found : Br = 49·25. Calc. for $C_7H_3O_4NBr_2$, Br = 49·20 per

cent.). This substance shows no depression of melting point on admixture with 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde. On oxidation with alkaline permanganate, an acid is formed melting at 230° (decomp.; corr.) which does not depress the melting point of 2 : 4-dibromo-6-nitro-3-hydroxybenzoic acid prepared either from 2 : 4-dibromo-6-nitro-*m*-cresol or from the dimercuri-derivative of 6-nitro-3-hydroxybenzaldehyde (see above).

In the expectation, which as shown above was not realised, that replacement of the two mercury residues in this compound by bromine would yield 2 : 6-dibromo-4-nitro-3-hydroxybenzaldehyde, which could be converted into the corresponding acid, the latter was prepared by oxidation of 2 : 6-dibromo-4-nitro-*m*-cresol with alkaline potassium ferricyanide, which gave rise to two substances, (*a*) the required acid, 2 : 6-*dibromo*-4-*nitro*-3-*hydroxybenzoic acid*, m. p. 209° (corr.) (Found : Br = 47·23. $C_7H_3O_5NBr_2$ requires Br = 46·89 per cent.), and (*b*) 4 : 6-dibromo-2-nitrophenol, m. p. 120—121° (Found : Br = 53·91. Calc., 53·84 per cent.); the formation of the latter affords an independent proof of the constitution of the acid.

Treatment of the dimercurated substance with excess of a 5 per cent. solution of iodine in 10 per cent. potassium iodide solution gives rise to a *di-iodo*-4-*nitro*-3-*hydroxybenzaldehyde* which crystallises from acetone in yellow needles, m. p. 122° (corr.) (Found : I = 60·91; C = 19·77, 19·98; H = 0·79, 0·74. $C_7H_3O_4NI_2$ requires I = 60·60; C = 20·05; H = 0·72 per cent.). On oxidation with alkaline permanganate, this is converted into a *di-iodo*-4-*nitro*-3-*hydroxybenzoic acid*, crystallising from benzene in small, yellow prisms, m. p. 249° (decomp.; corr.) (Found : I = 58·41. $C_7H_3O_5NI_2$ requires I = 58·37 per cent.).

In order to obtain some evidence of the position of the iodine atoms in this substance, 4-nitro-*m*-cresol prepared by Städel and Kolb's method (*Annalen*, 1890, **259**, 210) was treated with iodine and mercuric oxide in alcoholic solution. Under these conditions, it slowly deposits crystals of a *di-iodo*-4-*nitro*-m-*cresol*, melting at 110° (decomp.; corr.), but the substance is more readily obtained by boiling 4-nitro-*m*-cresol with iodine and iodic acid in dilute alcoholic solution (Found : I = 62·90. $C_7H_5O_3NI_2$ requires I = 62·69 per cent.). 4-Nitro-*m*-cresol on treatment with bromine and mercuric oxide in alcoholic solution gives 2 : 6-dibromo-4-nitro-*m*-cresol (Clause and Hirsch, *J. pr. Chem.*, 1889, [ii], **39**, 61), and by analogy the substance obtained by the action of iodine should be 2 : 6-di-iodo-4-nitro-*m*-cresol. On oxidation with alkaline potassium ferricyanide it is converted into an acid, m. p. 249° (decomp.; corr.), identical with the di-iodo-acid described above,

which should therefore be 2 : 6-di-iodo-4-nitro-3-hydroxybenzoic acid, indicating that the mercury residues in the original dimercuri-compound are in positions 2 and 6, as was expected, since mercury invariably enters in positions ortho or para with respect to the hydroxyl group, which in this series of compounds seems to determine the possibility of mercuration under the conditions described.

The monomercurated compound on treatment with iodine yields a *mono-iodo-4-nitro-3-hydroxybenzaldehyde* crystallising from acetone, or better from chloroform, in shining, yellow needles, m. p. 185° (corr.) (Found : I = 43·37, 43·54. $C_7H_4O_4NI$ requires I = 43·33 per cent.).

In order to remove any doubt as to the purity or identity of the 4-nitro-3-hydroxybenzaldehyde used in the mercuration experiments, it was oxidised, by means of alkaline permanganate, to the known 4-nitro-3-hydroxybenzoic acid, m. p. 235° (corr.), which was also obtained by oxidising 4-nitro-*m*-cresol with alkaline potassium ferricyanide. No trace of any other acid, such as 6-nitro-3-hydroxybenzoic acid, could be detected in the oxidation product of the aldehyde.

Using the general method with 2-nitro-3-hydroxybenzaldehyde (1 mol.) and mercuric acetate (2 mols.), a yellow precipitate forms as the reaction proceeds; this is filtered from the boiling solution from time to time to prevent "bumping." The first crops are amorphous and appear to be *hydroxymercuriacetoxymercuri-2-nitro-3-hydroxybenzaldehyde* (Found : Hg = 62·41. $C_9H_7O_7NHg_2$ requires Hg = 62·47 per cent.). In the later stages, as the concentration of acetic acid increases according to the equation $RH + Hg(O{\cdot}CO{\cdot}CH_3)_2 = R{\cdot}HgO{\cdot}CO{\cdot}CH_3 + CH_3{\cdot}CO_2H$, the solid is deposited in a crystalline condition and consists of diacetoxydimercuri-2-nitro-3-hydroxybenzaldehyde. Towards the end of the reaction, some reduction of the mercuric acetate takes place and the last crops are contaminated with mercurous acetate.

The product is purified by dissolving it in potassium hydroxide solution, filtering from mercurous oxide, then precipitating with carbon dioxide, and finally crystallising from acetic acid. Pale yellow needles of *diacetoxydimercuri-2-nitro-3-hydroxybenzaldehyde* are thus obtained (Found : Hg = 58·35. $C_{11}H_9O_8NHg_2$ requires Hg = 58·62 per cent.). This substance is insoluble in the usual organic solvents, but dissolves in formic, acetic, or propionic acid. It is slightly soluble in sodium hydroxide solution, but comparatively readily soluble in potassium hydroxide solution and from the latter hydrochloric acid precipitates *dichlorodimercuri-2-nitro-3-hydroxybenzaldehyde* as a pale green, gelatinous substance soluble in acetone

or alcohol (Found: Hg = 62·94. $C_7H_3O_4NCl_2Hg_2$ requires Hg = 62·96 per cent.). This decomposes at 236° (corr.).

When one molecular proportion of mercuric acetate is used, the main product is still the dimercurated compound, which separates as already described, but the mother-liquors on concentration deposit a yellow solid consisting of a mixture of mono- and di-mercurated products along with unchanged 2-nitro-3-hydroxybenzaldehyde. The solid is finely powdered, thoroughly extracted with ether to remove 2-nitro-3-hydroxybenzaldehyde, and the residual mercury compound fractionally crystallised from acetic acid, in which the mono-compound is the more soluble. Neither the mono- nor the di-acetoxymercuri-compound has a definite melting or decomposition point, so that analysis has to be resorted to as a means of controlling the progress of separation. *Acetoxymercuri-2-nitro-3-hydroxybenzaldehyde* crystallises from acetic acid in bundles of microscopic needles, which darken on heating, but do not melt at 300° (Found: Hg = 47·43. $C_9H_7O_6NHg$ requires Hg = 47·13 per cent.). The solution in potassium hydroxide on addition of hydrochloric acid gives a pale yellow precipitate of *chloromercuri-2-nitro-3-hydroxybenzaldehyde* which decomposes at about 207° (Found: Hg = 49·76. $C_7H_4O_4NClHg$ requires Hg = 49·89 per cent.).

On shaking the dimercurated compound with a slight excess of a cooled, freshly prepared 5 per cent. solution of bromine in alcohol, the mercury is removed and a dibromo-compound is obtained in 88 per cent. yield. This crystallises from chloroform in colourless prisms, m. p. 152·5° (decomp.; corr.) and is identical with the dibromo-compound obtained from the dimercuri-derivatives of 6-nitro-3-hydroxybenzaldehyde (p. 1053) and 4-nitro-3-hydroxybenzaldehyde (p. 1055). From the mother-liquors a little 2 : 4-dibromo-6-nitro-3-hydroxybenzoic acid, m. p. 230° (decomp.), is obtained. In this case, as in that of the dimercuri-derivative of 4-nitro-*m*-hydroxybenzaldehyde (p. 1056), replacement of the two mercury residues by bromine leads to interchange of position between the nitro-group and the bromine atom in position 6.

Treatment of the dimercuri-derivative with excess of a solution of iodine in potassium iodide yields a di-iodo-compound which crystallises from chloroform in bright yellow needles, m. p. 154·5° (corr.) (Found: C = 19·74; H = 0·89; I = 60·27. $C_7H_3O_4NI_2$ requires C = 20·05; H = 0·72; I = 60·60 per cent.).

This di-iodo-compound is not known and the authors have so far been unable to prepare it by this or any other method, which will yield it in sufficient quantity for determination of the position of the iodine atoms. There can, however, be very little doubt that

it is 4:6-*di-iodo*-2-*nitro*-3-*hydroxybenzaldehyde*, since in 2-nitro-3-hydroxybenzaldehyde only three positions (ortho, meta, and para with respect to the hydroxyl) are available for the entry of mercury. As already pointed out, no case is known in which mercury enters in a position meta to hydroxyl, and as two mercury residues enter in this case, it is almost certain that they enter in positions 4 and 6 as suggested in formula III (p. 1050).

The crude monomercurated product on similar treatment yields, together with some di-iodo-compound melting at 154·5°, a second iodo-compound melting at about 110° which is probably mono-iodo-2-nitro-3-hydroxybenzaldehyde, but owing to the very small quantity available it has not been possible to obtain it in a sufficiently pure condition for analysis.

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CXXII.—*The Isomerism of the Oximes. Part XVII. Some Bromo- and Nitro-substituted Mono- and Di-methoxybenzaldoximes.*

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THE present investigation is a continuation of those on the influence of negative groups on the stability of isomeric benzaldoximes. There are a number of substituted benzaldoximes from which the *syn*-isomeride cannot be prepared, but no underlying principle is apparent to indicate when this will be the case (Brady and Dunn, J., 1916, **109**, 667). The presence of a hydroxy-group or amino- or substituted amino-group in the nucleus appears to inhibit the formation of a *syn*-isomeride; ortho-substitution also seems to produce a hindering effect (compare Wentworth and Brady, J., 1920, **117**, 1040; Brady and Truszkowski, J., 1923, **123**, 2434). We have now studied 3-nitro-*p*-methoxy-, 3-bromo-*p*-methoxy-, 5-nitro-*o*-methoxy-, 5-nitro-3:4-dimethoxy-, 6-nitro-3:4-dimethoxy-, and 6-bromo-3:4-dimethoxy-benzaldoximes. In a number of cases, the oximes are known, but they have not been investigated from the point of view of stereoisomerism. The oximes prepared by the usual methods have the *anti*-configuration, this being determined by means of the acetyl derivative (Hantzsch, *Ber.*, 1891,

24, 13). Various methods of obtaining the *syn*-isomerides have been applied and a number of derivatives prepared in order to extend previous investigations on the carbanilino-compounds and the ethers.

Ciusa's work (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 721) on 3-nitro-*p*-methoxybenz*anti*aldoxime, its *syn*-isomeride, and a number of derivatives has been confirmed; our results, however, differ somewhat from his in details. Ciusa relied upon the formation of a benzyl ether different from that produced from the *anti*-oxime as a proof that he had obtained the *syn*-isomeride. This is at best a qualitative method which does not give much indication of the purity of the compound. We have now determined the configuration by the more trustworthy method involving the action of acetic anhydride (Hantzsch, *loc. cit.*).

3-Bromo-*p*-methoxybenz*anti*aldoxime readily gives a *syn*-isomeride, but no success attended our attempts to convert 5-nitro-*o*-methoxy-, 6-nitro-3 : 4-dimethoxy-, 6-bromo-3 : 4-dimethoxy-, and 5-nitro-3 : 4-dimethoxy-benz*anti*aldoximes. In all these cases, as in those of 6-nitro-3 : 4-methylenedioxy- and 2 : 4-dinitro-benz*anti*aldoximes (Brady and Dunn, J., 1915, **107**, 1862; Wentworth and Brady, *loc. cit.*), no hydrochloride was formed when solutions of the oximes in organic solvents were treated with dry hydrogen chloride. The failure to obtain hydrochlorides from the first three oximes was attributed to ortho-substitution, but this explanation became untenable when it was found that 5-nitro-3 : 4-dimethoxybenz*anti*aldoxime did not yield a hydrochloride or a *syn*-isomeride, behaviour all the more unexpected because 5-bromo-3 : 4-dimethoxybenz*anti*aldoxime readily underwent conversion (Wentworth and Brady, *loc. cit.*); indeed it is the ease with which this bromo-compound could be converted into a comparatively stable *syn*-isomeride whereas, until quite recently, 3 : 4-dimethoxybenz*anti*aldoxime could not (compare Brady and Dunn, J., 1923, **123**, 1799), that suggested the investigation of negatively substituted compounds.

Experimental.

3-Nitro-*p*-methoxybenz*anti*aldoxime, m. p. 166° (Ciusa, *loc. cit.*, gives m. p. 170°) was warmed (5 grams) with 20 c.c. of acetic anhydride at 30° until dissolved, left for a short time, the excess of anhydride decomposed by excess of 2*N*-sodium carbonate, and the precipitate crystallised from alcohol with the addition of animal charcoal, when *acetyl-3-nitro-*p*-methoxybenzantialdoxime* was obtained in colourless, hexagonal plates, m. p. 130° (Found : N = 11·9. $C_{10}H_{10}O_5N_2$ requires N = 11·8 per cent.). On hydrolysis

with hot 2*N*-sodium hydroxide, it yielded the original oxime, which had, therefore, the *anti*-configuration.

3-*Nitro*-p-*methoxybenz*syn*aldoxime.*—We could not obtain this compound by Beckmann's process (*Annalen*, 1909, **365**, 201; compare Ciusa, *loc. cit.*), but prepared it by Dunstan and Thole's method (P., 1911, **27**, 233) or by precipitation of the hydrochloride from a solution of the oxime in boiling chloroform (compare Brady and Dunn, J., 1923, **123**, 1783), the former being the better owing to the rather sparing solubility of the oxime in chloroform. The *anti*-oxime was ground into a thin paste with concentrated hydrochloric acid and the suspension saturated for 10 minutes with hydrogen chloride. The mixture was then poured slowly into a large excess of well-stirred sodium carbonate solution, and the precipitated *syn*-oxime collected, washed, and crystallised from acetone and water. It is difficult to obtain a product melting higher than 161° by this means, but a further crystallisation from acetone and water followed by crystallisation from benzene gave a compound melting at 164—166° (Ciusa gives 168—170°).

The two isomerides melt at almost the same temperature, as is the case with the two isomeric *m*-nitrobenzaldoximes, but at a lower temperature on admixture.

Acetyl-3-*nitro*-p-*methoxybenz*syn*aldoxime*, prepared by means of acetic anhydride at room temperature, crystallised from acetone and water in colourless needles, m. p. 115° (Found: N = 11·9. $C_{10}H_{10}O_5N_2$ requires N = 11·8 per cent.). It was decomposed by 2*N*-sodium hydroxide, yielding 3-nitro-*p*-methoxybenzonitrile on gentle warming, and ammonia and 3-nitro-*p*-methoxybenzoic acid (as sodium salt) on boiling.

Benzyl Ethers of 3-*Nitro*-p-*methoxybenzaldoxime.*—The action of benzyl chloride on the sodium salts of the isomeric oximes was investigated and the results of Ciusa were confirmed. The melting point of the *N*-ether was, however, found to be 203°, whilst Ciusa gives 195°.

O-*Methyl Ether of* 3-*Nitro*-p-*methoxybenz*anti*aldoxime.*—Ten grams of 3-nitro-*p*-methoxybenz*anti*aldoxime, dissolved in 55 c.c. of 2*N*-sodium hydroxide, were shaken with 7 grams of methyl sulphate, crystals of the *O*-methyl ether, mixed probably with a small amount of the *N*-ether, soon separating. These were collected and on crystallisation from alcohol gave the O-*methyl* ether in colourless, rectangular plates, m. p. 120° (Found: N = 13·4. $C_9H_{10}O_4N_2$ requires N = 13·3 per cent.). The residue from the reaction mixture and the alcoholic mother-liquor from the crystallisation were distilled in steam, but no *N*-ether could be isolated from the non-volatile portion.

*N-Methyl Ether of 3-Nitro-*p*-methoxybenzaldoxime.*—3-Nitro-*p*-methoxybenz*syn*aldoxime was methylated in the same way as the *anti*-isomeride. The solid which separated was crystallised from alcohol, when the *N-ether* was obtained in yellow prisms, m. p. 180° (Found : N = 13·4; MeO = 15·0. $C_9H_{10}O_4N_2$ requires N = 13·3; 1MeO = 14·8 per cent.). The residual liquor from the crystallisation of the *N*-ether on distillation in steam gave a small quantity of a colourless, crystalline compound having a higher melting point than the *O*-methyl ether of the *anti*-isomeride. This was probably the *O*-methyl ether of the *syn*-isomeride, but the amount available was too small for further investigation.

*Carbanilino-3-nitro-*p*-methoxybenz*anti*aldoxime.*—A solution of the *anti*oxime (1 mol.) and phenylcarbimide (1 mol.) in dry ether was kept in the dark for 3 days, when a few crystals appeared and, on shaking, the *carbanilino*-derivative rapidly separated. Crystallised from alcohol, it was obtained in colourless prisms melting and decomposing at 128° (Found : N = 13·3. $C_{15}H_{13}O_5N_3$ requires N = 13·3 per cent.). On hydrolysis by hot 2*N*-sodium hydroxide, the compound dissolved completely, no diphenylcarbamide being formed, and carbon dioxide precipitated the original oxime from the alkaline solution.

*Carbanilino-3-nitro-*p*-methoxybenz*syn*aldoxime* was immediately precipitated when an ethereal solution of the *syn*-oxime was treated with phenylcarbimide (1 mol.). It crystallised from acetone and water in colourless, rectangular plates melting and decomposing at 117° (Found : N = 13·5. $C_{15}H_{13}O_5N_3$ requires N = 13·3 per cent.). On warming with 2*N*-sodium hydroxide, aniline and 3-nitro-*p*-methoxybenzonitrile were formed; on prolonged boiling, ammonia was evolved, the compound dissolved completely, and carbon dioxide then precipitated a very small quantity of 3-nitro-*p*-methoxybenz*anti*aldoxime, whilst mineral acids gave 3-nitro-*p*-methoxybenzoic acid in good yield. The production of a little *anti*-oxime in the hydrolysis was probably due to isomeric change of a small amount of the carbanilino-*syn*-derivative into the corresponding *anti*-compound during the preliminary stages of the reaction, as this change takes place very readily.

*3-Bromo-*p*-methoxybenzaldehyde.*—Considerable difficulty was experienced in brominating *p*-methoxybenzaldehyde, the methods previously described giving poor yields (compare Cahours, *Annalen*, 1845, **56**, 308; Walther and Wetzlich, *J. pr. Chem.*, 1854, **61**, 198; Johnson and Benglio, *J. Amer. Chem. Soc.*, 1912, **34**, 1061), but the following process was satisfactory, the yield being 80 per cent. A solution of *p*-methoxybenzaldehyde and the calculated quantity of bromine in glacial acetic acid (freshly prepared by twice freezing

the commercial acid) was heated under reflux with a few crystals of iodine until the evolution of hydrogen bromide ceased, when the mixture was poured into water. The precipitated oil was separated, the aqueous layer extracted with ether, the oil and extract were together washed with 2*N*-sodium hydroxide, dried over potassium carbonate, and the solvent was evaporated, leaving the aldehyde in white crystals, m. p. 51—52°.

3-*Bromo*-p-*methoxybenz*an*tialdoxime*, prepared in the usual way from 20 grams of the aldehyde, crystallised from alcohol in colourless, slender needles, m. p. 118° (Found : N = 6·2. $C_8H_8O_2NBr$ requires N = 6·1 per cent.). The *acetyl* derivative, prepared by the method given in the preceding section, crystallised from alcohol in thin, rectangular plates, m. p. 82° (Found : N = 5·1. $C_{10}H_{10}O_3NBr$ requires N = 5·2 per cent.). It was readily hydrolysed by warm 2*N*-sodium hydroxide, yielding the sodium derivative of the original oxime, the *anti*-configuration of which was thus established.

3-*Bromo*-p-*methoxybenzonitrile*, prepared by boiling the *anti*-oxime for some hours under reflux with excess of acetic anhydride, and isolated in the usual way, crystallised from alcohol in colourless needles, m. p. 122° (Found : N = 6·9. C_8H_6ONBr requires N = 6·6 per cent.), and gave 3-bromo-*p*-methoxybenzoic acid (Gattermann, *Ber.*, 1899, **32**, 1121) on hydrolysis.

3-*Bromo*-p-*methoxybenz*syn*aldoxime*, prepared from 10 grams of the *anti*-oxime by the hydrochloric acid method described above, crystallised from acetone and water in colourless plates, m. p. 134° (Found : N = 6·3. $C_8H_8O_2NBr$ requires N = 6·1 per cent.). When treated successively with cold acetic anhydride and sodium carbonate solution, it gave 3-bromo-*p*-methoxybenzonitrile, its *syn*-configuration being thus indicated.

O-*Benzyl Ether of* 3-*Bromo*-p-*methoxybenz*an*tialdoxime*.—To a solution of 5 grams of 3-bromo-*p*-methoxybenz*anti*aldoxime in warm absolute alcohol a solution of 0·5 gram of sodium in alcohol was added, when the sodium salt of the oxime separated. The mixture was heated on the water-bath with 2·7 grams of benzyl chloride for ½ hour. The O-*benzyl* ether that separated on cooling was washed with water and crystallised from alcohol, and formed colourless, thin, rectangular plates, m. p. 82° (Found : N = 4·7. $C_{15}H_{14}O_2NBr$ requires N = 4·4 per cent.).

N-*Benzyl Ether of* 3-*Bromo*-p-*methoxybenzaldoxime*.—3-Bromo-*p*-methoxybenz*syn*aldoxime was treated in a similar way to the *anti*-oxime, but the sodium salt did not separate. Benzyl chloride was added to the cold solution and the mixture left at the ordinary temperature over-night. The N-*benzyl* ether which separated was

washed with water and crystallised from alcohol, and obtained in yellow, rectangular plates, m. p. 151° (Found: N = 4·7. $C_{15}H_{14}O_2NBr$ requires N = 4·4 per cent.).

O-Methyl Ether of 3-*Bromo*-p-*methoxybenzantialdoxime*.—Prepared in the same way as the corresponding ether of the 3-nitro-oxime, this compound crystallised from alcohol in colourless plates, m. p. 76° (Found: N = 6·0; MeO = 24·7. $C_9H_{10}O_2NBr$ requires N = 5·7; 2MeO = 25·0 per cent.). From the filtered reaction mixture and the mother-liquors from the crystallisation was obtained a very small amount of the *N*-ether described below.

N-Methyl Ether of 3-*Bromo*-p-*methoxybenzaldoxime*.—The *syn*-oxime was treated in the same way as the *anti*-oxime, except that 2*N*-potassium hydroxide was used, as the sodium salt was sparingly soluble in water. The ethereal extract of the product was evaporated, the residue distilled in steam, the non-volatile portion cooled and extracted with ether, the solvent removed, and the residue crystallised from benzene and light petroleum. The compound retained solvent rather tenaciously, but after keeping for a few days in an evacuated desiccator it melted sharply at 108° and consisted of colourless plates (Found: MeO = 12·6. $C_9H_{10}O_2NBr$ requires MeO = 12·5 per cent.). The steam distillate was extracted with ether, but the only product obtained was somewhat impure aldehyde formed probably by the hydrolysis of the *N*-ether.

Carbanilino-3-bromo-p-*methoxybenzantialdoxime*.—The crystals obtained by keeping a solution of 5 grams of 3-bromo-*p*-methoxybenz*anti*aldoxime and 2·6 grams of phenylcarbimide in dry ether in the dark for 3 days were crystallised from benzene and light petroleum, when the *carbanilino*-compound separated in colourless needles, m. p. 92° (Found: N = 8·3. $C_{15}H_{13}O_3N_2Br$ requires N = 8·0 per cent.). The compound was hydrolysed by heating on the water-bath for 2 hours with 2*N*-sodium hydroxide. A trace of ammonia was evolved and there was a marked odour of a carbylamine, and an insoluble residue of diphenylcarbamide. Aniline was detected in the alkaline filtrate, and on saturating this with carbon dioxide a copious precipitate of 3-bromo-*p*-methoxybenz*anti*aldoxime was obtained, the *anti*-configuration of the carbanilino-derivative being thus established.

The filtrate from the original reaction mixture was freed from ether, but the residue could not be separated into pure products; on hydrolysis, however, a considerable amount of ammonia was given off, indicating the presence of the carbanilino-*syn*-compound, which would yield first nitrile and then ammonia and the acid.

Carbanilino-3-bromo-p-*methoxybenzsynaldoxime*. — When equimolecular quantities (as above) of the *syn*-oxime and phenyl-

carbimide were mixed in dry ether the carbanilino-compound was at once precipitated. Crystallised from acetone and water, it formed colourless, rectangular plates melting and decomposing at 104° (Found: N = 8·1. $C_{15}H_{13}O_3N_2Br$ requires N = 8·0 per cent.). On hydrolysis as above, ammonia was evolved, no oxime was precipitated by carbon dioxide, but acids gave 3-bromo-*p*-methoxybenzoic acid; no diphenylcarbamide was obtained.

5-*Nitro*-o-*methoxybenz*anti*aldoxime*, prepared from 16 grams of 5-nitro-*o*-methoxybenzaldehyde (Schnell, *Ber.*, 1884, **17**, 1382) in the usual way, crystallised from alcohol in colourless plates, m. p. 183° (Found: N = 14·5. $C_8H_8O_4N_2$ requires N = 14·3 per cent.). Its *anti*-configuration was established by the regeneration of the oxime on hydrolysis of the *acetyl* derivative, which was prepared in the usual way and crystallised from alcohol in colourless prisms, m. p. 160° (Found: N = 12·0. $C_{10}H_{10}O_5N_2$ requires N = 11·8 per cent.).

Attempts to prepare 5-*Nitro*-o-*methoxybenz*syn*aldoxime*.—When a solution of 5-nitro-*o*-methoxybenz*anti*aldoxime in ether was saturated with hydrogen chloride, the oxime, not a hydrochloride, was precipitated. Solutions in cold or boiling chloroform gave no precipitate with hydrogen chloride, whilst from solutions in boiling benzene or boiling xylene the oxime was again precipitated (compare Brady and Dunn, J., 1923, **123**, 1784). The oxime was treated with concentrated hydrochloric acid and the solution saturated with hydrogen chloride, but on pouring the clear solution so obtained into excess of aqueous sodium carbonate the *anti*-oxime was precipitated. Five grams of 5-nitro-*o*-methoxybenzaldehyde were heated in absolute alcoholic solution with a slight excess of hydroxylamine hydrochloride at 50° for 3 hours, but the substance which separated on cooling was the pure *anti*-oxime (Beckmann, *loc. cit.*).

6-*Nitro*-3:4-*dimethoxybenz*anti*aldoxime*.—This compound has been described by Bamberger and Elger (*Annalen*, 1910, **371**, 336), but its configuration has not been determined. The best method of preparing the compound was as follows: 10 grams of 6-nitro-3:4-dimethoxybenzaldehyde (Pschorr and Sumuleanu, *Ber.*, 1899, **32**, 3412) were dissolved in the minimum of hot alcohol, 4 grams of hydroxylamine hydrochloride dissolved in a small quantity of water were added, followed by 60 c.c. of 2*N*-sodium hydroxide, the resulting solution was diluted somewhat and filtered, and the oxime precipitated with carbon dioxide and crystallised from alcohol.

Acetyl-6-*nitro*-3:4-*dimethoxybenz*anti*aldoxime* prepared by means of acetic anhydride, crystallised from alcohol in pale yellow leaflets, m. p. 152° (Found: N = 10·5. $C_{11}H_{12}O_6N_2$ requires N = 10·5 per cent.). Hydrolysis with 2*N*-sodium hydroxide in the usual way

regenerated the original oxime, which has therefore the *anti*-configuration.

5-Nitro-3 : 4-dimethoxybenzaldehyde.—Considerable difficulty was experienced in preparing this aldehyde. Pschorr and Stöhrer's method (*Ber.*, 1902, **35**, 4399) or slight modifications of it gave very poor yields, not more than 5 to 10 per cent. of the original material being converted, and in all only 2 grams of pure 5-nitro-3 : 4-dimethoxybenzaldehyde being obtained. Methyl sulphate and methyl toluene-*p*-sulphonate were ineffective, and Irvine's method (J., 1901, **79**, 668) resulted in oxidation. Two methods were finally discovered which gave satisfactory yields of the required aldehyde. (*a*) Finely powdered 5-nitrovanillin was suspended in dry ether and treated with two equivalents of diazomethane in ether. Vigorous effervescence occurred and the 5-nitrovanillin disappeared. The solution was filtered, the solvent removed, and the product washed with dilute sodium hydroxide solution to remove any unchanged 5-nitrovanillin, and crystallised from alcohol. Although the yield was satisfactory, the toxic nature of diazomethane was objectionable and the presence of more than two molecular proportions of the reagent led to reaction with the aldehyde group and the formation of *5-nitro-3 : 4-dimethoxyacetophenone*, which crystallises from alcohol in pale yellow needles, m. p. 89° (Found : N = 6·3. $C_{10}H_{11}O_5N$ requires N = 6·2 per cent.). (*b*) The silver salt of 5-nitrovanillin, prepared from the sodium salt and excess of silver nitrate solution in artificial light, was thoroughly washed, being kept as much as possible in the dark. After drying for several days in an evacuated desiccator in the dark, it was finely powdered and suspended in dry ether and an excess of methyl iodide. After a week the precipitate was separated and the ethereal solution evaporated, when an almost quantitative yield of crude 5-nitro-3 : 4-dimethoxybenzaldehyde was obtained which could be easily purified by crystallisation from alcohol.

5-Nitro-3 : 4-dimethoxybenzantialdoxime, prepared in an analogous manner to the 6-nitro-compound, crystallised from alcohol in minute, colourless plates, m. p. 151° (Found : N = 12·5. $C_9H_{10}O_5N_2$ requires N = 12·4 per cent.). The *acetyl* derivative, prepared in the usual way, crystallised from cold acetone and water in colourless plates, m. p. 115° (Found : N = 10·5. $C_{11}H_{12}O_6N_2$ requires N = 10·5 per cent.); on hydrolysis with 2*N*-sodium hydroxide, it yielded the original oxime.

Acetyl-6-bromo-3 : 4-dimethoxybenzantialdoxime.—The best method of preparing 6-bromo-3 : 4-dimethoxybenzaldehyde is that described by Pschorr (*Annalen*, 1912, **391**, 32), good results being obtained if the acetic acid used as solvent is anhydrous. The oxime was

prepared in an analogous way to that of the 6-nitro-compound above and was acetylated in the usual way. The *acetyl* derivative crystallised from alcohol in colourless leaflets, m. p. 140° (Found: N = 4·7. $C_{11}H_{12}O_4NBr$ requires N = 4·6 per cent.). On hydrolysis with 2*N*-sodium hydroxide, it regenerated the original oxime.

Attempts to obtain syn-*Isomerides from* 5-*Nitro-*, 6-*Nitro-*, and 6-*Bromo*-3 : 4-*dimethoxybenz*anti*aldoximes*.—The various methods employed with 5-nitro-*o*-methoxybenz*anti*aldoxime above were tried with these three oximes, but in no case was a hydrochloride obtained. Treatment with concentrated hydrochloric acid, saturation with hydrogen chloride, and subsequent pouring of the reaction product into sodium carbonate solution regenerated the original oxime, whilst Beckmann's method (*loc. cit.*) yielded the *anti*-isomeride.

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CXXIII.—*Influence of Intensive Drying on Inner Equilibria.*

By ANDREAS SMITS.

THE interesting observations made by H. B. Baker and Mrs. Baker (J., 1912, **101**, 2339) on the influence of intensive drying on the boiling points of nitrogen trioxide and nitrogen tetroxide are of great importance for the theory of allotropy, and the author has already directed attention to their significance in a recent paper (*Z. physikal. Chem.*, 1922, **100**, 477). The following passage from this paper may be quoted as setting forth the author's views at the time:

"Diese Untersuchungen Bakers sind darum so interessant, weil sie dartun, dass die inneren Umsetzungen in einem unären System bei intensiver Trocknung stark gehemmt, oder was wahrscheinlicher ist, volkommen zum Stillstand gebracht werden können, so dass durch intensive Trocknung aus einem unären System ein Pseudosystem erhalten wird, dessen Bestandteile z.B. durch fraktionierte Destillation u.s.w. von einander getrennt werden können.

"Weil wir kaum annehmen können, dass bei der intensiven Trocknung eine Verschiebung des inneren Gleichgewichtes stattgefunden hat, lässt sich aus den Resultaten Bakers schliessen, dass bei seinen Versuchen während der Erhitzung schon eine fraktionierung stattgefunden hat und dass also der beim intensiv getrockneten Trioxyd erhaltene Siedepunkt sich auf eine Flüssigkeit bezieht, welche während der Erhitzung bis zur Siedepunkttemperatur schon zum Teil verdampft war. Die grösste Wichtigkeit der Resultate

Bakers liegt nun meines Erachtens darin, dass sie uns lehren, dass die intensive Trocknung wahrscheinlich, wenn nicht das schönste, doch eines der schönsten Mittel sein wird, um die Komplexe Natur der unären Phasen eines allotropen Stoffes zu beweisen. Und wenn, wie sich erwarten lässt, die inneren Umsetzungen bei intensiver Trocknung in der Tat zum Stillstand kommen, so wird es uns gelingen können, aus einer anfanglich unären Phase, die Pseudokomponente in reinen Zustand ab zu trennen um das Pseudosystem, völlig zu studieren."

The view taken was that by intensive drying the inner transformations in a unary phase are stopped, the inner equilibrium is fixed, and a mixture is obtained which on distillation generally will give a distillate with a lower boiling point and a residue with a higher boiling point than the original liquid. It was concluded that the boiling points observed by Baker were abnormally high because the liquid mixture, before reaching the boiling point, had already partly evaporated.

Subsequent to the publication of Baker's later investigations on the properties of extremely dry liquids (J., 1922, **121**, 568), the author discussed these results in a chapter of his "Theory of Allotropy," and considered, in view of these new experiments, whether the original explanation set out above might be regarded as adequate, or should be supplemented by the assumption that the inner equilibrium is *first displaced and then fixed.* The following quotations from the chapter mentioned will explain the position adopted :

"The important question still remains : What really happens in the drying process ? It might at first sight appear permissible to explain the results obtained by assuming that in the reversible change $\alpha \rightleftarrows \beta$ the reaction $\leftarrow$ becomes stationary sooner than the reverse change $\rightarrow$, as a result of which a phase arises containing an *excess* of the β type of molecule or this molecular species *exclusively;* but it is then tacitly assumed that a trace of moisture can displace the inner equilibrium to a very considerable extent, the thermodynamical significance of which is, that a very large amount of work is necessary in order to withdraw the last traces of water from the substance, and this is *not improbable.*"

"It is clear that a small elevation of the boiling point could have been explained from the circumstance that the fixation temperature was generally lower than the boiling point. Here, however, the observed changes are of such a kind that they must undoubtedly be attributed to the operation of entirely different causes. In the case of the elevation of the melting point of sulphur, or of iodine, it might rather be expected that these much smaller temperature

increases are perhaps to be explained by the displacement which the inner equilibrium in the solid phase undergoes with change of temperature."

"The question what actually happens during intensive drying, *whether it is merely a fixation or whether displacement of the inner equilibrium first occurs, followed by fixation,* has not yet been answered with certainty from the results of Baker's experiments. It can, however, easily be answered. If the vapour pressure of the liquid phase changes solely as a result of intensive drying, this change must take place before any portion of the liquid is distilled off, and thus it is certain that during the drying process the inner equilibrium has been displaced. If, however, the vapour pressure remains constant and a decrease in the vapour pressure first appears after a portion of the liquid has been removed by distillation, intensive drying then acts merely by fixing the inner equilibrium state. The same question can also be answered by determining the boiling point, if the boiling point is observed when the intensively dried liquid is boiled under a reflux condenser and the volume of the vapour is kept small. If fixation only occurs, the boiling point will not change; but if a portion of the liquid is distilled off, the boiling point will then rise immediately. If, however, the inner equilibrium is also displaced, the boiling point will change before any liquid is distilled off. My impression is that this actually occurs."

These somewhat detailed references to the author's published views are necessary, since a communication by G. N. Lewis, entitled "Extremely dry liquids," has recently appeared (*J. Amer. Chem. Soc.*, 1923, **45**, 2836), in which an explanation of Baker's observations is offered corresponding exactly with that originally put forward by the author and embodied in the foregoing quotations. It may again be emphasised that in the author's "Theory of Allotropy" the original form of his explanation (see *loc. cit.*, *Z. physikal. Chem.*) was supplemented by the assumption that by the drying process the inner equilibrium can be displaced, *an assumption which is not in contradiction with thermodynamic considerations.* Lewis, however, makes no reference in his paper to these previously published expressions of the author's views, either in their earlier or later form.*

The question whether the drying process is a fixation, or a displacement of the inner equilibrium, followed by fixation, can be

* The only paper which Lewis refers to is a later communication, dealing with the influence of intensive drying on reactivity (*Proc. K. Akad. Amsterdam*, 1923, **26**, 266). In this communication, in which I referred to my explanation in the original and extended forms, I placed the latter distinctly in the foreground, but it was not my intention to exclude the original form of the explanation in general, as given in my book.

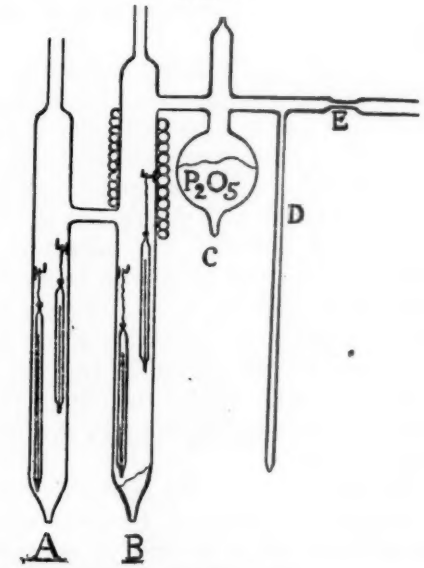
settled only by actual investigation, and experiments were carried out with the object of throwing light on this matter. As indicated above, the determination of the vapour pressure provides the best method of studying the question. Further, the vapour tension should be measured at the drying temperature, since a difference between the drying temperature and the temperature at which the vapour tension is measured might possibly have significance.

EXPERIMENTAL.

The results which I wish to communicate here have regard to the temperature of the boiling liquid and the coexisting vapour of benzene, which had been dried by pure phosphorus pentoxide. And, although the drying process has only lasted about $1\frac{1}{2}$ years, I am able to record a very distinct change, and to get an indubitable answer to the question whether the dried benzene behaves as a mixture or not.

The apparatus used had the following form.

FIG. 1.



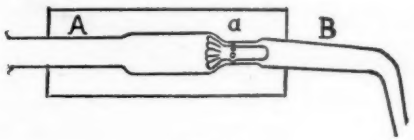


FIG. 2.

Two wide tubes, *A* and *B*, 2 cm. in diameter, each containing two thermometers, one for reading the temperature of the liquid and

the other for reading that of the vapour, were connected by a tube $1\frac{1}{2}$ cm. wide in H form. Farther a bulb, *C*, was fused to tube *B*, and to this tube a capillary, *D*, and a tube, *E*.

The apparatus having been cleaned and dried, all tubes except *E* were sealed off, and *E* was connected with the mercury diffusion pump to find if all joints were absolutely air-tight. Such a test is always necessary and if it was thus showed that the apparatus was tight, the vertical tube of the bulb, *C*, was sealed to the phosphorus pentoxide distilling tube. I have modified the method of preparing pure phosphorus pentoxide which was used by Baker (private communication) in two respects.

The distillation tube is 75 cm. long and 2·5 cm. in diameter. The wider part has a diameter of 3·5 cm. In the narrowed portion, a glass stopper, provided with points, is placed, so that whilst free channels are left round it, there is no danger of impure phosphorus pentoxide passing into *B* during the operation of filling the bulb. This distilling tube is placed in an electric furnace and the bent part of the tube *B* is sealed to the vertical tube of the bulb *C* in the apparatus (Fig. 1).

The free end of the tube *A* (Fig. 2) is connected by a rubber stopper with an apparatus in which oxygen (freed from traces of hydrogen by heating at 500° in a quartz tube containing platinum) was dried first by two worm tubes containing pure sulphuric acid and by two tubes, 1 m. in length, filled with glass and phosphorus pentoxide.

Whilst oxygen dried in this way was passing through the distilling tube, this tube, part *B* included, was heated to redness. After cooling, the distilling tube was filled with commercial phosphorus pentoxide as rapidly as possible by the method devised by C. J. Baker, namely, by forming the pentoxide into plugs by pressing a glass tube into the bottle and forcing the plug out with a glass rod which fits it like a plunger. During the filling the oxygen current was passing through the distilling tube in the opposite direction, namely, from right to left.

After filling, the distilling tube was connected with the apparatus for drying the oxygen, by means of a rubber stopper, and whilst the oxygen was sent through at the rate of two or three bubbles, or nearly 0·35 c.c., per second, the tube was heated by the electric furnace to 220°.

During the distillation of phosphorus pentoxide into the part *B*, every part of the sealed boiling apparatus was heated to redness whilst, by closing the other tubes, the oxygen was forced to go through the heated bulb or tube. This is a very important part of the experiment, since the surface of the glass is covered by a film of moisture. Besides this, as Baker has pointed out, the glass frequently

contains streaks or capillaries which may get filled with water during the cleaning process, and it requires a high temperature and a long time to remove the last traces of water from these capillaries.

During this heating, the open tube was connected by a short rubber tube with a U-tube filled with phosphorus pentoxide, and a wash-bottle with strong sulphuric acid. After sufficient heating, each tube was sealed off in turn, and another was heated. The last was tube *E* and this was, of course, not sealed off but remained connected to the U-tube and sulphuric acid wash-bottle. Before sealing off the tubes *A* and *B*, the thermometers were suspended from glass points by platinum wires and then the tubes were heated once more, but only to 100°.

The sublimed pentoxide is deposited in the part *B*, and since this part is bent downwards the pure pentoxide can be introduced into the bulb *C* by tapping, or by heating the pure pentoxide once more very carefully with a burner, and distilling into the bulb *C*. By the last method the pentoxide is obtained in a *very fine* and *extremely active* state.

When enough pure pentoxide had been introduced, tube *E* was sealed off and the capillary tube, *D*, opened under previously boiled mercury. Now the upper end of tube *B* was opened once more and very pure benzene, dried for several weeks by commercial and distilled phosphorus pentoxide, was introduced into *B*, whilst the dry oxygen was going in the opposite direction. After cooling the tube *B* in a bath of solid carbon dioxide and alcohol, the upper end of this tube was again sealed off, and after the oxygen current was stopped, also the vertical tube of the bulb *C*.

Between the two horizontal side-tubes a cooling spiral of composition tube was wound round the tube *B* and connected with the water supply. By regulating this cooling it was possible to distil the benzene from tube *B* into tube *A*, without allowing it to pass into bulb *C* and also without its running down the thermometer that was hanging in the vapour. Since the capillary tube, *D*, was opened under previously boiled mercury, the boiling point could be determined at 1 atmosphere pressure.

June 2nd, 1922.—The experiment showed that during the whole distillation the temperature of the boiling liquid and the temperature of the vapour remained constant at 80°.

The benzene having been distilled back into *A*, the capillary tube, *D*, was sealed off just above the mercury surface and the apparatus then allowed to stand for some months, whilst the cooling by the metal spiral tube caused a continuous movement of the vapour. After almost 3 months' standing, probably owing to the

relatively large quantity of very fine phosphorus pentoxide, we got the impression that a small change could already be noticed.

August 25th, 1922.—During the distillation of the boiling benzene the temperature of the liquid rose to 81·5° and the temperature of the vapour to 81°.

Six months later, we were quite certain that there was a very distinct effect, produced by the drying.

February 23rd, 1923.—The temperature of the boiling and distilling liquid showed a rise up to 87°, whilst the temperature of the vapour rose to 85°.

After this experiment, a crack developed while the capillary tube was being again sealed off, and although the capillary tube was immediately repaired a small quantity of moist air had entered.

This accident had a very interesting result, which was completely in agreement with a result of Baker. After a month, the experiment was repeated, with the following result.

March 23rd, 1923.—The temperature of the boiling and distilling liquid during the distillation rose only to 81·5° and the temperature of the vapour to 80·9°. *Consequently the effect attained after 9 months' intensive drying had almost completely disappeared.* The drying was continued and after 4 months the drying effect had become perceptible again.

June 29th, 1923.—End-boiling point of the liquid, 83°. Temperature of the vapour, 81°.

Now the apparatus was allowed to stand more than 7 months and the experiment was then repeated.

February 7th, 1924.—During the distilling of the boiling benzene, the temperature of the liquid rose to 86·6°, whilst the temperature of the vapour was 84·8°. There was still one-quarter of the original quantity of the liquid, but the bulb of the lower thermometer was no longer covered by the liquid. The distillation was continued and when nearly one-eighth of the original liquid was left, the temperature of the vapour had risen to 87·7°. If I could have determined the temperature of the small quantity of the liquid which was still boiling, it would certainly have been nearly 89°.

As Baker has already mentioned (J., 1923, **123**, 1223), I visited his laboratory in December, 1922, and had the pleasure of repeating his former determinations and making new ones. During this visit, Prof. Baker was kind enough to sacrifice, at my request, a small fractionating flask of dried benzene, in order to see if, as I had already predicted, a separation of the pseudo-components by distillation could be realised. There was a thermometer in the vapour only and although the liquid was evaporated, before boiling had begun, the temperature of the vapour rose from 81° to 87°.

This experiment showed that distillation effected a separation of the pseudo-components.

The experiments made in my laboratory and described above confirm the results obtained in co-operation with Prof. Baker, and moreover they prove that this result can be obtained after 1 year of intensive drying.

The question whether the drying process is a fixation of the inner equilibrium or a displacement of the inner equilibrium followed by a fixation, could not be answered by these experiments. A future communication will deal with this question. We also hope to describe the way in which we have prepared the glass apparatus and the circulating method used to get a more rapid intensive drying.

We have also begun an extensive investigation of the influence of intensive drying on the transition point, the melting point, the vapour tension of the solid and liquid states and on the electrical resistance of the liquid phase of a great number of substances. Among them, those substances of which Baker found that the chemical activity disappeared on intensive drying occupy an important place.

Summary.

1. It has been shown that the explanation of Baker's experiments given by G. N. Lewis was put forward by the author more than two years ago.

2. In agreement with experiments done in co-operation with Prof. Baker, it is found that dried benzene behaves as a mixture and that this behaviour could be observed after one year's drying.

THE UNIVERSITY, AMSTERDAM. [*Received, February 13th*, 1924.]

CXXIV.—*The Isomorphism of the Amides and Substituted Amides of Dichloro- and Chloroiodo-acetic Acids, and of Chlorobromo- and Chloroiodo-acetic Acids.*

By PHYLLIS V. MCKIE.

THE property of isomorphism, that is, the formation of a continuous series of solid solutions, was shown (McKie, J., 1923, **123**, 2213) to be characteristic of the fusion mixtures of corresponding pairs of the amides and substituted amides of dichloro- and chlorobromo-acetic acids, and further examination of the fusion curves of similar pairs of the corresponding derivatives of (1) dichloro- and chloroiodo-acetic acids, and of (2) chlorobromo- and chloroiodo-acetic acids indicates, in general, analogous behaviour.

Of the two types of curves previously obtained (*loc. cit.*, p. 2214), mixtures of the anilides and of the benzylamides of dichloro- and chloroiodo-acetic acids, and of the amides of dichloro- and chloroiodo-acetic acids, and of chlorobromo- and chloroiodo-acetic acids conform to type (1); in all other instances type (2) is displayed, although the fall to a minimum value is in some cases very slight.

Experimental.

Preparation of Materials.—Methods similar to those described for derivatives of dichloro- and chlorobromo-acetic acids (*loc. cit.*) were used for the corresponding derivatives of chloroiodoacetic acid, with the exception that the acid chloride obtained by the interaction of αβ-dichlorovinyl ether with iodine monochloride could not be fractionated previous to use, and hence the isolation and purification of the chloroiodo-compounds were more troublesome.

Chloroiodoacetomethylamide, m. p. 107·5° (Found : N = 5·96. CHClI·CO·NHMe requires N = 5·98 per cent.). *Chloroiodoacetoethylamide*, m. p. 79·4° (Found : N = 5·63. CHClI·CO·NHEt requires N = 5·64 per cent.). *Chloroiodoacetobenzylamide*, m. p. 120·5° (Found : N = 4·49. CHClI·CO·NH·CH_2Ph requires N = 4·51 per cent.). *Chloroiodoacetomethylanilide*, m. p. 88·0° (Found : N = 4·50. CHClI·CO·NMePh requires N = 4·51 per cent.). *Chloroiodoacetoethylanilide*, m. p. 92·3° (Found : N=4·30. CHClI·CO·NEtPh requires N = 4·30 per cent.).

Determination of the Melting Point.—The method employed was that previously described (*loc. cit.*).

In the following tables the observed melting points of mixtures of corresponding pairs of compounds are given, together with the melting points calculated on the assumption that they lie on a straight line joining the melting points of the constituents; in all cases *a* denotes the molecular percentage of the chloroiodo-compound.

Dichloro- and chloroiodo-acetamides.

	Melting points.	
a.	Obs.	Cal.
0	98·5°	—
9·03	99·7	102·2°
21·16	101·4	107·3
39·6	105·8	114·9
59·12	112·8	123·0
80·16	124·4	131·8
100·0	140·0	—

Chlorobromo- and chloroiodo-acetamides.

	Melting points.	
a.	Obs.	Cal.
0	123·0°	—
8·18	123·4	124·0°
18·9	125·0	125·4
40·34	127·3	128·1
50·24	128·4	129·3
78·6	132·4	132·9
100·0	135·6	—

Dichloro- and chloroiodo-acetomethylamides.

	Melting points.	
a.	Obs.	Cal.
0	79·0°	—
11·34	75·5	82·2°
19·39	75·0	84·5
23·21	73·5	85·6
32·03	72·1	88·1
41·35	73·2	90·8
51·96	80·0	93·8
69·9	90·6	98·9
86·76	100·1	103·7
100·0	107·5	—

Chlorobromo- and chloroiodo-aceto-methylamides.

a.	Melting points. Obs.	Cal.
0	93·1°	—
9·5	92·6	94·4°
25·93	92·9	96·8
38·49	93·9	98·6
51·87	95·3	100·4
64·36	97·4	102·3
74·84	98·8	103·7
100·0	107·5	—

Dichloro- and chloro-iodo-acetoethyl-amides.

a.	Melting points. Obs.	Cal.
0	67·8°	—
5·1	59·5	68·4°
26·8	56·7	70·9
39·7	54·5	72·4
51·4	53·3	73·8
67·8	56·1	75·6
73·98	58·6	76·4
88·86	68·1	78·1
100·0	79·4	—

Chlorobromo- and chloroiodo-aceto-ethylamides.

a.	Melting points. Obs.	Cal.
0	67·8°	—
12·73	64·8	69·3°
24·07	65·1	70·6
42·2	65·3	72·7
58·05	66·8	72·5
74·2	69·3	76·4
28·6	65·0	71·1
100·0	79·4	—

Dichloro- and chloro-iodo-acetobenzyl-amides.

0	96·2°	—
16·05	96·1	100·1°
28·3	95·2	103·1
36·94	95·3	105·1
45·8	97·3	106·3
50·4	99·6	108·4
60·1	103·5	110·8
80·4	111·1	115·7
100·0	120·5	—

Chlorobromo- and chloroiodo-aceto-benzylamides.

0	105·0°	—
14·38	106·8	109·4°
28·37	108·4	109·4
45·0	110·4	111·9
51·07	111·2	112·9
61·79	113·4	114·6
80·04	116·0	117·4
100·0	120·5	—

Dichloro- and chloro-iodo-acetanilides.

0	117·7°	—
19·39	114·0	122·4°
28·3	107·0	124·6
35·03	106·2	126·3
40·4	108·0	127·6
41·13	108·0	127·8
60·36	117·9	132·3
77·0	127·6	136·6
100·0	142·3	—

Eutectic mixture, m. p. 105·2°, containing 36·3 per cent. of chloro-iodoacetanilide.

Chlorobromo- and chloroiodo-acet-anilides.

0	116·8°	—
9·9	116·8	119·3°
20·4	118·6	122·0
43·7	122·4	127·9
49·56	123·7	129·4
60·37	126·1	132·2
78·36	131·4	136·8
100·0	142·3	—

Dichloro- and chloro-iodo-acetomethyl-anilides.

0	69·9°	—
20·11	68·3	73·54°
39·6	68·4	77·92
60·87	68·8	79·92
80·19	75·5	84·42
100·0	88·0	—

Chlorobromo- and chloroiodo-aceto-methylanilides.

0	86·6°	—
8·6	85·0	86·7°
29·8	81·2	87·0
31·8	80·5	87·0
44·63	79·3	87·2
60·45	79·2	87·4
66·07	79·2	87·5
77·3	80·0	87·7
100·0	88·0	—

Dichloro- and chloro-iodo-acetoethyl-anilides.

0	54·4°	—
9·06	53·7	57·9°
19·67	54·1	61·9
40·31	61·6	69·7
59·57	71·8	76·5
79·86	81·4	84·7
100·0	92·3	—

Chlorobromo- and chloroiodo-aceto-ethylanilides.

0	56·4°	—
9·7	56·3	59·9°
21·16	60·0	64·8
34·9	63·9	68·9
46·88	68·8	73·2
59·6	72·9	77·8
62·8	73·9	78·9
77·1	80·0	84·1
100·0	92·3	—

In the following table the divergence from the straight-line curve occasioned by the presence of the several substituted amido-groups is represented in order of decreasing magnitude.

Derivatives of dichloro- and chlorobromo-acetic acids.	Derivatives of dichloro- and chloroiodo-acetic acids.	Derivatives of chloro-bromo- and chloroiodo-acetic acids.
–NHPh.	–NHPh.	–NPhMe.
–NHMe.	–NHEt.	–NHEt.
–NPhEt.	–NHMe.	–NHPh.
–NPhMe.	–NPhMe.	–NHMe.
–NH·CH_2Ph.	–NH·CH_2Ph.	–NPhEt.
–NHEt.	–NPhEt.	–NH·CH_2Ph.
–NH_2.	–NH_2.	–NH_2.

In each series the mixtures of pairs of unsubstituted acetamides show a smaller deviation from the straight-line curve than do mixtures of any other pair in the same series. The generalisation previously made (*loc. cit.*), that the phenyl group causes the maximum deviation from the straight-line curve, is borne out in the series of the dichloro- and chloroiodo-acetic acid derivatives where the fusion curve of the melting points of mixtures of the two acetanilides breaks away altogether from the isomorphous type and shows a marked eutectic. The greater tendency to approach the straight-line curve, caused in each case by the substitution of the corresponding chlorobromo- for the dichloro-derivative, is particularly marked in this case, where the fusion curve of mixtures of chlorobromo- and chloroiodo-acetanilides shows no minimum value lower than the melting point of either component.

Hence isomorphism, or the formation of mixed crystals in all proportions between corresponding pairs of amides and substituted amides of dichloro-, chlorobromo-, and chloroiodo-acetic acids is displayed by all mixtures of such derivatives of dichloro- and chlorobromo-acetic acids, and of chlorobromo- and chloroiodo-acetic acids. In the corresponding series of derivatives of dichloro- and chloroiodo-acetic acids, a break in the fusion curve of mixtures of dichloro- and chloroiodo-acetanilides, and the realisation of a curve of the eutectic type, indicate in these mixtures the absence of a continuous series of solid solutions. In all other mixtures examined, the formation of such a series of solid solutions is maintained.

The author desires to express her thanks to Mr. Holland Crompton for much advice and criticism.

NOTE.—I am indebted to Dr. Knaggs for permission to publish the following facts.—Crystallographic evidence points to a closer isomorphism between dichloro- and chlorobromo-acetoethylamides than between dichloroacetoethylanilide and dichloroacetomethylanilide. The abnormal effect caused by the group –NHMe (McKie,

loc. cit.) is possibly accounted for by the fact that, of the compounds which Dr. Knaggs has examined, this compound crystallises in the orthorhombic system, whilst the other members conform to the monoclinic system, although a certain amount of resemblance between them is shown in crystallographic elements.

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REGENT'S PARK, N.W. 1. [*Received, February 1st*, 1924.]

CXXV.—*Studies in the Anthracene Series. Part VIII.*

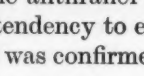
By EDWARD DE BARRY BARNETT and MARCUS AURELIUS MATTHEWS.

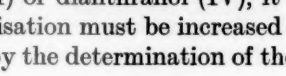
THE additive compounds of nitric acid with anthracene-1- and 2-sulphonic acids, like that with anthracene itself, are too unstable to be isolated in the pure state, and readily change into the 9-nitroanthracenesulphonic acids. In view of the publications of Battegay and Brandt (*Bull. Soc. Ind. Mulhouse*, 1923, **89**, 365) and of Battegay and Huebner (*Bull. Soc. chim.*, 1923, [iv], **33**, 1094), it is thought desirable to give a short account of our experiments on the reduction of anthraquinonesulphonic acids.

These acids are readily reduced by tin or iron and hydrochloric acid, and yield the corresponding anthronesulphonic acids. We have not oriented our products, as Battegay and Huebner (*loc. cit.*) have stated that they are engaged on this problem. It is remarkable that none of our anthronesulphonic acids when enolised with pyridine passes into a sultone, although in the case of anthranol-1 : 5-disulphonic acid there must be a phenolic hydroxyl group in the *peri*-position to one of the sulpho-groups.

All the anthronesulphonic acids on oxidation pass into the corresponding dianthrones. Since dianthrone itself is very stable to oxidation in acid solution (it can be recrystallised from boiling concentrated nitric acid), we hoped to be able to obtain the corresponding chlorodianthrones by treating the sulphonic acids with chlorine in hydrochloric acid solution, a method which has proved very useful in the anthraquinone series. This expectation has not been fulfilled, as in every case oxidation took place with the production of a chlorinated anthraquinone. Since the oxidation of an anthrone (I) or dianthrone (II) is always preceded by enolisation

to the anthranol (III) or dianthranol (IV), it seemed probable that the tendency to enolisation must be increased by the sulpho-groups. This was confirmed by the determination of the p_H values of aqueous


(I.)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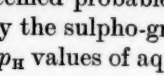
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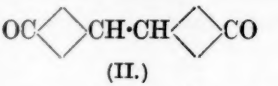
(IV.)

solutions of the sodium salts, the determination being made in the usual way by measuring the *E.M.F.* of a hydrogen electrode placed in the solution against a saturated calomel electrode. As a check on the method, the p_H value of a solution of sodium anthracene-1 : 8-disulphonate was determined under similar conditions, and in *N*/382-solution was found to be 9·75.

Anthraquinonesulphonic acids are converted into stable anthrone-sulphonic acids by sodium hyposulphite and therefore are useless as catalysts for the reduction of dyes by this agent (Battegay and Brandt, *loc. cit.*). We have found that anthraquinonesulphonic acids are rapidly reduced to the corresponding anthraquinols by sodium sulphide, and that the reduction shows very little tendency to go beyond this stage. The anthraquinonesulphonic acids, in particular the α-acids, consequently act as powerful catalysts in reductions with sodium sulphide, and the colours of azo-dyes which remain unaffected by boiling with sodium sulphide alone are rapidly discharged in presence of an anthraquinonesulphonic acid; even resistant dyes such as Ice Claret (diazotised α-naphthylamine coupled on the fibre with β-naphthol) are reduced in the course of about three minutes. Tartrazine and the stilbene dyes such as Direct Yellow and Chrysophenine remain unaffected.

Experimental.

Anthrone- and Dianthrone-sulphonic Acids.—Commercial anthraquinonesulphonic acid or one of its salts (50 grams), dissolved in boiling water (750—1000 c.c. and 250—400 c.c. in the case of the mono- and di-sulphonic acid, respectively) was treated with iron filings (25—30 grams) and concentrated hydrochloric acid (75 c.c.). If tin and hydrochloric acid are used, a tin salt is formed from which the metal cannot be removed by hydrogen sulphide. The reaction appeared to be finished in about 20 minutes, but was usually prolonged for another 15 minutes to ensure complete reduction. Prolonged boiling is to be avoided, as the large amount

of iron salt then formed renders the purification of the product troublesome. After reduction, the solution was filtered hot, diluted with a saturated solution of sodium chloride, the product, collected after cooling, was dissolved in boiling 2*N*-sodium hydroxide, the iron removed with hydrogen sulphide, and the filtrate faintly acidified with hydrochloric acid and treated with a saturated solution of sodium chloride. For analysis, the sodium salts were repeatedly crystallised from water.

The aniline anthrone- and dianthrone-sulphonates separated from boiling concentrated aqueous solutions of the sodium salts, acidified with hydrochloric acid, on treatment with aniline hydrochloride in about 50 per cent. excess, and were obtained in almost quantitative yield after cooling. After purification, they were analysed by titration with sodium hydroxide, phenolphthalein being used as an indicator except in the case of aniline anthrone-1 : 8-disulphonate, for which no indicator was required. These salts, unlike the aniline anthraquinonesulphonates (Perkin and Sewell, *J. Soc. Chem. Ind.*, 1923, **42**, 27T), have no definite melting points.

The *dianthronesulphonic acids* were prepared from the sodium anthronesulphonates and sodium peroxide in cold aqueous solution; the crystals obtained on acidification were repeatedly crystallised from water. The crude *dianthrone*-1 : 5 : 1′ : 5′-*tetrasulphonic acid* was resinous, but dissolved slowly on boiling with dilute hydrochloric acid. The solution was treated with a saturated solution of sodium chloride and on cooling deposited crystals of the *sodium* salt. It was found extremely difficult to obtain products which did not give the anthraquinol test.

Sodium 9(or 10)-anthrone-	Appearance.	Yield (grams).	S% (calc. value in brackets).	p_H and normality of soln.
1-Sulphonate.	—	42	10·90 (10·81)	4·9; *N*/251
2-Sulphonate.	Pale yellow needles from aq. alc.	41	10·87 (10·81)	5·2; *N*/234
1 : 5-Disulphonate.	Dark copper-coloured plates.	28	16·03 (16·08)	5·0; *N*/287
1 : 8-Disulphonate.	Straw-yellow needles.	30	16·11 (16·08)	5·26; *N*/123
Sodium dianthrone-				
ββ′-Disulphonate.	Yellow crystals.	—	10·65 (10·84)	5·37; *N*/139
1 : 5 : 1′ : 5′-Tetrasulphonate.	Orange crystals containing $1H_2O$.	—	15·94 (15·76)	5·4; *N*/117
aaa′a′-Tetrasulphonate.	Orange crystals.	—	16·31 (16·12)	6·0; *N*/85

The anthronesulphonic acids in neutral or acid aqueous solution are almost colourless, but become yellow or orange on the addition of a trace of alkali. The change in colour of the 1 : 8-*disulphonic acid* is so marked that this acid can be used as an indicator.

Aniline 9(or 10)-anthrone-	Appearance.	Behaviour on heating.	Analysis (calc. % in brackets).
1-Sulphonate.	Pink crystals.	Darkened at 280°. Black liquid at 283°.	$C_{14}H_{10}O_4S$ = 74·2 (74·7)
2-Sulphonate.	Straw-yellow needles.	Darkened at 295°. M. p. 304—309° (decomp.).	$C_{14}H_{10}O_4S$ = 74·8 (74·7)
1 : 5-Disulphonate.	Yellow prisms.	Darkened at 295°. Not melted at 330°.	$C_{14}H_{10}O_7S_2$ = 65·2 (65·5)
1 : 8-Disulphonate.	Orange needles containing $2H_2O$.	Not melted at 325°.	$C_{14}H_{10}O_7S_2$ = 61·3 (61·4) H_2O = 6·33 (6·25)
Aniline dianthrone-			
$\beta\beta'$-Disulphonate.	Brownish-yellow needles.	Darkened at 300°. M. p. 317° (decomp.).	$C_{28}H_{18}O_8S_2$ = 74·4 (74·6)
1 : 5 : 1′ : 5′-Tetrasulphonate.	Yellow plates, falling to powder in vac. desicc.	Darkened. Not melted at 320°.	$C_{28}H_{18}O_{14}S_4$ = 65·1 (65·5)
$\alpha\alpha'\alpha'$-Tetrasulphonate.	Orange-yellow needles.	—	$C_{28}H_{18}O_{14}S_4$ = 65·2 (65·5)

Nitroanthracenesulphonic Acids.—The anthracenesulphonic acids were prepared by reducing the corresponding anthraquinonesulphonic acids with zinc dust and ammonia, and were isolated by salting out with sodium chloride. In all cases the crude product was boiled for some time with aqueous sodium hydroxide to expel ammonia, and the solution then treated with hydrogen sulphide to precipitate small quantities of zinc. The aniline salts were prepared in the usual way, as it was thought that they might be useful for identification purposes. The 2-sulphonic acid did not give an aniline salt under the usual conditions. The other sulphonic acids all gave well-crystallised aniline salts which could be titrated, but which did not melt below 330° (*Aniline anthracene-1-sulphonate.* Found : $C_{14}H_{10}O_3S$ = 73·3; $C_{20}H_{17}O_3NS$ requires $C_{14}H_{10}O_3S$ = 73·5 per cent. *Aniline anthracene-1 : 5-disulphonate.* Found : $C_{14}H_{10}O_6S_2$ = 64·9; $C_{26}H_{24}O_6N_2S_2$ requires $C_{14}H_{10}O_6S_2$ = 64·5 per cent. *Aniline anthracene-1 : 8-disulphonate.* Found : $C_{14}H_{10}O_6S_2$ = 64·7; $C_{26}H_{24}O_6N_2S_2$ requires $C_{14}H_{10}O_6S_2$ = 64·5 per cent.).

9(or 10)-*Nitroanthracene-1-sulphonic Acid.*—Ten grams of sodium anthracene-1-sulphonate, suspended in 25 c.c. of glacial acetic acid, were treated with 2·3 c.c. of nitric acid (*d* 1·42) and, after 15 minutes, the filtered solution was diluted with ether, when a viscous mass separated. This became solid on triturating with ether and undoubtedly consisted of an additive compound of anthracenesulphonic acid with nitric acid, but was too unstable to be purified. It was therefore boiled with pyridine and the resulting yellow powder

recrystallised several times from water, when it was obtained in slender, yellow needles (Found: S = 10·45. $C_{14}H_9O_5NS$ requires S = 10·56 per cent.).

9(or 10)-*Nitroanthracene-2-sulphonic Acid.*—The nitration was carried out as above. The additive compound, which could not be purified, was treated with pyridine, the product dissolved in water, and the sodium salt precipitated by sodium chloride. Recrystallised several times from glacial acetic acid containing a little water, it formed pale yellow crystals which retained water and acetic acid very obstinately (Found: N = 3·96, 3·97; S = 8·64. $C_{14}H_8O_5NSNa,2H_2O$ requires N = 3·88; S = 8·86 per cent.).

Neither anthracene-1 : 5-disulphonic acid nor anthracene-1 : 8-disulphonic acid is nitrated under the above conditions; at a higher temperature, the corresponding anthraquinonesulphonic acid is produced.

Summary.

1. The anthraquinonesulphonic acids when reduced in acid solution pass readily into the corresponding anthronesulphonic acids, from which the dianthronesulphonic acids can be obtained by oxidation.

2. The anthraquinonesulphonic acids are reduced by sodium sulphide in aqueous solution to the anthraquinolsulphonic acids. They therefore act as catalysts in reduction reactions with sodium sulphide, and the colour of many azo-dyes is rapidly discharged by heating with a solution of sodium sulphide containing an anthraquinonesulphonic acid.

3. The anthracenemonosulphonic acids form additive compounds with nitric acid which are too unstable to be isolated, but which pass into the corresponding nitroanthracenesulphonic acid on treatment with pyridine. Sulpho-groups in the α-position hinder the formation of such additive compounds, and no nitro-compound could be obtained from anthracene-1 : 5- or 1 : 8-disulphonic acid.

In conclusion, the authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of this research. The thanks of one of them (M. A. M.) are also due to the Department of Scientific and Industrial Research for a grant which has enabled him to take part in this work.

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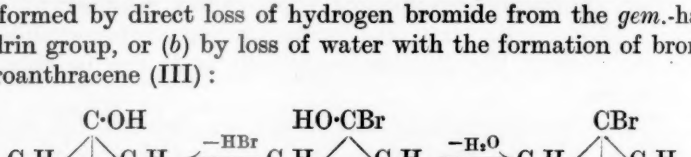
ALDGATE, E.C. 3. [*Received, January 2nd,* 1924.]

CXXVI.—*Studies in the Anthracene Series. Part IX.*

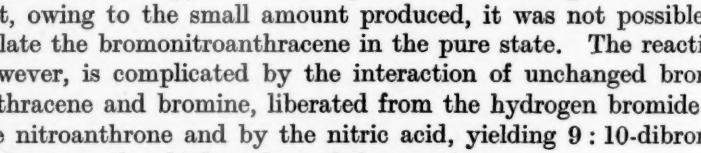
By EDWARD DE BARRY BARNETT and JAMES WILFRED COOK.

SUBSTITUTION reactions in the anthracene series in which the *meso*-carbon atoms are involved usually take the form of an additive reaction, with subsequent re-establishment of the "bridge" by loss of water, hydrogen halide, etc. Evidence of the formation of additive compounds, which are usually too unstable to be isolated in the pure state, has frequently been obtained (see, for example, Barnett, Cook, and Matthews, J., 1923, **23**, 1994; Barnett and Cook, *ibid.*, p. 2631). In this connexion it seemed of interest to examine the behaviour of 9-bromoanthracene towards nitric acid, as re-establishment of the "bridge" in the intermediate additive compound (I) might take place (*a*) by loss of hydrogen bromide with the formation of nitroanthranol (II), which would at once enolise to nitroanthrone, or alternatively nitroanthrone might be formed by direct loss of hydrogen bromide from the *gem.*-halohydrin group, or (*b*) by loss of water with the formation of bromonitroanthracene (III):



Both reactions appear to take place, the former predominating, but, owing to the small amount produced, it was not possible to isolate the bromonitroanthracene in the pure state. The reaction, however, is complicated by the interaction of unchanged bromoanthracene and bromine, liberated from the hydrogen bromide by the nitroanthrone and by the nitric acid, yielding 9 : 10-dibromoanthracene, the chief product of the reaction.

The action of chlorine on 9-bromoanthracene might yield dichloroanthracene (V) and chlorobromoanthracene (VI), by way of the additive compound (IV), but chlorobromoanthracene was the only



compound isolated. Minor reactions apparently take place, for the crude product melts at a decidedly lower temperature than that obtained by chlorinating with sulphuryl chloride.

The reaction between anthracene and bromine, like that with nitric acid (Barnett, Cook, and Matthews, *loc. cit.*), is a reversible one. If the additive compound is treated with ice-cold dilute hydriodic acid, or with compounds such as phenol which take up bromine very readily, anthracene is regenerated. The decomposition of dibromodihydroanthracene on warming yields dibromoanthracene, in addition to the monobromo-compound, which is the main product of the reaction. Since monobromoanthracene is more easily separated from anthracene than from dibromoanthracene, its preparation is facilitated by carrying out the decomposition of the additive compound in presence of a little phenol. This not only prevents the formation of dibromoanthracene, but also catalyses the reaction involving loss of hydrogen bromide. The action of both chlorine and bromine on 9-bromoanthracene is much more rapid than on anthracene; in neither case could the intermediate additive compounds be isolated.

Experimental.

9 : 10-Dibromo-9 : 10-dihydroanthracene (anthracene dibromide) was prepared by a modification of Perkin's method (*Chem. News*, 1876, **34**, 144; *Bull. Soc. chim.*, 1877, [ii], **27**, 464). A solution of bromine (5 c.c.) in carbon disulphide (100 c.c.) was slowly added to 18 grams of finely powdered anthracene suspended in 200 c.c. of carbon disulphide, cooled in a freezing mixture. No hydrogen bromide was evolved, and after ½ hour the solid was collected and washed with cold carbon disulphide and with cold ether (yield 32 grams).

Anthracene dibromide slowly evolves hydrogen bromide at the ordinary temperature, but the reaction is not complete even after 3 days.

Reversion of Anthracene Dibromide to Anthracene.—(*a*) A suspension of the dibromide (2 grams) in 25 c.c. of glacial acetic acid, to which had been added 5 c.c. of hydriodic acid (*d* 1·70), was kept in ice-water for 3 hours with occasional shaking. After being washed with acetic acid and recrystallised from pyridine, the product was free from bromine and melted at 217°, alone or when mixed with an authentic sample of anthracene.

(*b*) A solution of 3 grams of phenol in 30 c.c. of dry toluene containing the dibromide (6·8 grams) in suspension was kept for 12 hours at the ordinary temperature, warmed gently on the water-bath, and cooled. The solid was recrystallised from pyridine, and identified as anthracene by the method of mixed melting points.

Dibromoanthracene from Anthracene Dibromide.—Pure anthracene

dibromide (10 grams) was heated on the water-bath for 1½ hours, the product extracted with 250 c.c. of boiling alcohol, and the residue repeatedly crystallised from chloroform. The dibromoanthracene was identified by the method of mixed melting points.

9-*Bromoanthracene.*—Anthracene dibromide (50 grams), suspended in 250 c.c. of dry toluene containing 0·5 gram of phenol, was kept at the ordinary temperature for 4 days in a flask provided with a calcium chloride tube, and then slowly heated to 50°. The clear solution obtained after about 2 hours was heated on the boiling water-bath for ½ hour, and the toluene removed with steam; the solid, recrystallised from 1250 c.c. of alcohol, melted at 98—99°. The yield, 31·7 grams together with a further 4 grams obtained from the concentrated alcoholic liquors, amounted to 94 per cent. of the theoretical.

9-*Chloro*-10-*bromoanthracene.*—(*a*) 9-Bromoanthracene (2 grams), dissolved in 10 c.c. of carbon disulphide, was treated at 0° with 0·55 gram of chlorine in 5 c.c. of carbon disulphide. Hydrogen chloride was at once evolved and crystals separated. These, after being washed with ether, sintered at 180° and melted at 201—207°. They were purified by repeated crystallisation from chloroform, pyridine, and methyl ethyl ketone (Found: Cl + Br = 39·7. $C_{14}H_8ClBr$ requires Cl + Br = 39·7 per cent.).

9-*Chloro*-10-*bromoanthracene* forms slender, lemon-yellow needles, m. p. 207°. Its solutions show an intense bluish-violet fluorescence.

(*b*) 9-Bromoanthracene (2 grams), suspended in 10 c.c. of chloroform, reacted almost at once with 2 c.c. of sulphuryl chloride. After subsidence, the whole was warmed for 2 hours, cooled, and the solid washed with ether; it then melted at 204—207°. It was purified by recrystallisation from chloroform and was proved to be 9-chloro-10-bromoanthracene by the method of mixed melting points.

Action of Nitric Acid on 9-*Bromoanthracene.*—9-Bromoanthracene (5 grams), suspended in 50 c.c. of glacial acetic acid, was treated with 1·4 c.c. of nitric acid (*d* 1·42) with stirring and cooling. Most of the bromoanthracene dissolved and after a few minutes crystals began to separate. The solid was collected after 2 hours and washed with acetic acid and with ether. It weighed 2 grams and after recrystallisation from acetic acid and from pyridine was identified as 9 : 10-dibromoanthracene by the method of mixed melting points.

The acetic acid liquors from the above nitration were diluted with hydrochloric acid, and the solid which separated was washed with water and boiled with a dilute solution of sodium hydroxide. Part dissolved to form a blood-red solution and this was filtered into hot dilute acetic acid; the yellow precipitate was recrystallised

from carbon disulphide and the product, almost colourless needles, decomp. 143°, was identified with 9-nitroanthrone by the preparation of an acetate, which melted at 182—183° alone or when mixed with an authentic sample of 9-nitroanthranyl acetate. The part which was insoluble in sodium hydroxide was recrystallised from pyridine and from acetic acid and then melted very indefinitely at about 210°. It contained both nitrogen and bromine and probably consisted of bromonitroanthracene mixed with some dibromoanthracene, but owing to the small amount obtained it was not further examined.

Summary.

1. Improved methods for preparing anthracene dibromide and monobromoanthracene are described.

2. The reaction between anthracene and bromine is a reversible one.

3. Monobromoanthracene when treated with chlorine gives chiefly chlorobromoanthracene.

4. Monobromoanthracene when treated with nitric acid gives dibromoanthracene, nitroanthrone, and possibly a little bromonitroanthracene.

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this research. Their thanks are also due to the South Metropolitan Gas Company for a gift of anthracene.

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ALDGATE, E.C.3. [*Received, January 14th,* 1924.]

CXXVII.—*The Isomerism of the Oximes. Part XVIII. The Action of* 2 : 4-*Dinitrochlorobenzene on some Isomeric Aldoximes.*

By OSCAR LISLE BRADY and RICHARD TRUSZKOWSKI.

THE evidence in favour of the Hantzsch-Werner theory of the isomerism of oximes furnished by their ethers rests on a wholly solid foundation only in the case of the three methyl derivatives of *m*-nitrobenzaldoxime (Gabriel, *Ber.*, 1882, **15**, 3060; Goldschmidt and Kjellin, *Ber.*, 1890, **23**, 2171; Brady and Dunn, J., 1913, **103**, 1625; compare also Brady and Dunn, this vol., p. 291); in other cases, at least one of the isomeric ethers is a liquid. 2 : 4-Dinitrochlorobenzene, which readily yields solid ethers on treatment with sodium alkyloxides, gave promise of being a valuable

reagent for the preparation of other series of solid, isomeric ethers. Its reactions with the sodium salts of *syn*- and *anti*-aldoximes, however, took unexpected courses.

Werner (*Ber.*, 1894, **27**, 1655) and Brady and Thomas (J., 1922, **121**, 2106) had previously prepared 2 : 4-dinitrophenyl ethers from benz*anti*aldoxime, *m*-nitrobenz*anti*aldoxime, and cinnam*anti*-aldoxime; many others are described in the experimental section below. These ethers, to which Werner (*loc. cit.*), on evidence not wholly convincing, attributed the constitution of *O*-ethers, $R{\cdot}CH{:}N{\cdot}O{\cdot}C_6H_3(NO_2)_2$, are not readily attacked by concentrated hydrochloric acid, but are, unlike the *O*-alkyl ethers, easily hydrolysed by warm 5 per cent. alcoholic sodium hydroxide with the formation of sodium dinitrophenoxide and the corresponding nitriles. The formation of the latter compounds, if the analogy of the acetyl and other derivatives is to be accepted, indicates that the dinitrophenyl compounds have the *syn*-configuration (compare Brady and McHugh, J., 1923, **23**, 1190):

$$\begin{matrix} R{\cdot}C{\cdot}H \\ \| \\ N{\cdot}O{\cdot}C_6H_3(NO_2)_2 \end{matrix} \longrightarrow (NO_2)_2C_6H_3{\cdot}OH + RCN.$$

It is noteworthy that the dinitrophenyl ethers from *o*-methoxy- and *p*-hydroxy-benz*anti*aldoximes behave in this way, although previously no *syn*-derivatives of these oximes had been obtained. In accordance with previous practice, we have designated all the dinitrophenyl ethers we have studied as *syn*-compounds, and previous statements with regard to those derived from benz*anti*-aldoxime, *m*-nitrobenz*anti*aldoxime, and cinnam*anti*aldoxime must be modified. The interaction of dinitrochlorobenzene and the sodium salts of the *anti*-oximes is therefore analogous to that of diphenylcarbamyl chloride, where the diphenylcarbamyl compound was found to be a *syn*-derivative in all the cases investigated (Brady and Dunn, J., 1913, **103**, 1614).

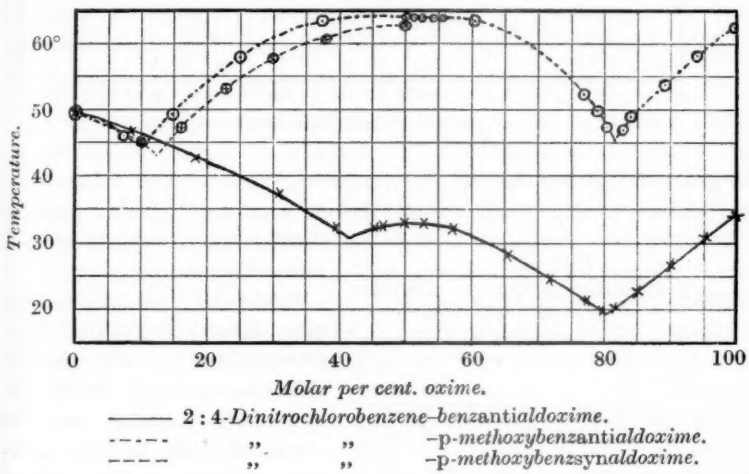
The main products of the action of 2 : 4-dinitrochlorobenzene on the sodium salts of the *syn*-oximes were the corresponding aldehyde and sodium dinitrophenoxide. Hydroxylamine could not be detected and therefore it is difficult at present to give a satisfactory explanation of the mechanism of the reaction. It may involve the formation of an *N*-ether. The reaction is being further investigated.

The reaction has been performed with benz*syn*aldoxime, *p*-methoxybenz*syn*aldoxime, and cinnam*syn*aldoxime, and also with acetaldoxime and heptaldoxime which, like all purely aliphatic aldoximes, are regarded as having the *syn*-configuration. It appears to be a general one and the action of dinitrochlorobenzene might accordingly be used as an alternative method for the determination

of the configuration of aldoximes. The method would have the advantage that it can be carried out rapidly with small quantities of material, since the identification of the products is simple, *anti*-oximes giving a crystalline ether and *syn*-oximes an aldehyde and sodium dinitrophenoxide. There appear, however, to be a few cases in which the sodium salt of an *anti*-oxime does not give an ether, for example, 3-bromo-*p*-dimethylamino- and *o*-hydroxybenz*anti*aldoximes.

The fusion curves of binary mixtures of 2 : 4-dinitrochlorobenzene with four characteristic oximes have been constructed, two of the oximes being ones which readily give *syn*-isomerides and two which are known only in the *anti*-form (Figs. 1—3).

FIG. 1.



Benz*anti*aldoxime and *p*-methoxybenz*anti*aldoxime (Fig. 1) form well-defined additive compounds with an equimolecular quantity of 2 : 4-dinitrochlorobenzene. When *p*-methoxybenz*syn*aldoxime or the *anti*-isomeride was added to 2 : 4-dinitrochlorobenzene, the fusion curve followed practically the same course in both cases (Fig. 1) and the respective compounds obtained by fusing together equimolecular quantities of the two components were found to be identical. Since very different products are obtained by the action of dinitrochlorobenzene on the sodium salts of the two isomerides, it seems probable that, under the conditions of the experiment, conversion of the *syn*- into the *anti*-isomeride takes place.

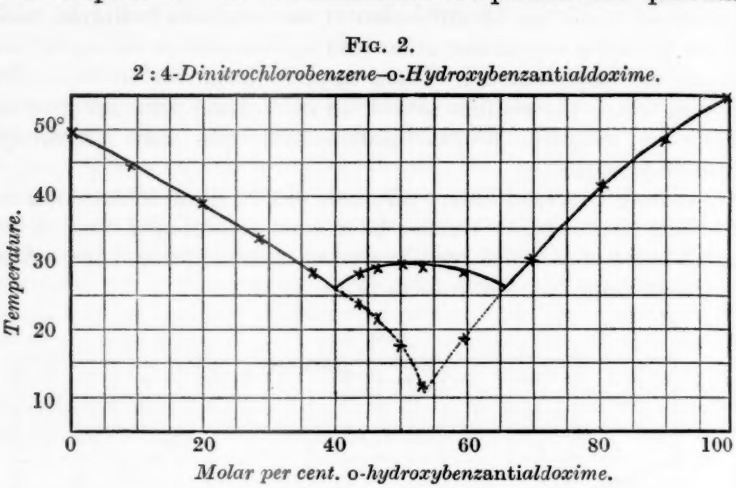
The interesting results obtained in the case of *o*-hydroxybenz*anti*aldoxime (Fig. 2) are described in the experimental section.

The fusion diagram for *o*-methoxybenz*anti*aldoxime and 2 : 4-di-

nitrochlorobenzene (Fig. 3) shows no indication of the formation of a compound of the two substances in equimolecular quantities,

FIG. 2.

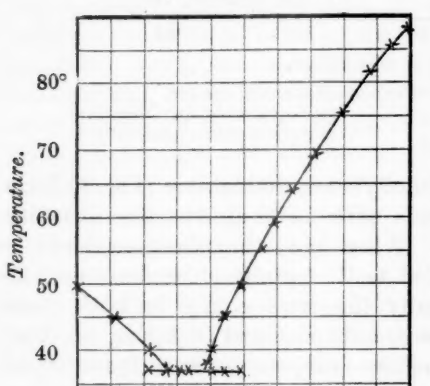
2 : 4-*Dinitrochlorobenzene–*o*-Hydroxybenz*antial*doxime.*



though the flat portion of the curve at the eutectic temperature may indicate the transient formation of a compound of 2 mols. of dinitrochlorobenzene with 1 mol. of oxime.

FIG. 3.

2 : 4-*Dinitrochlorobenzene–*o*-Meth-oxybenz*antial*doxime.*



Since the first two oximes give relatively stable *syn*-isomerides by the hydrochloride method whilst the last two oximes can be obtained only in the *anti*-form, these results suggest that there is some foundation for the views previously put forward in this series of papers that the formation of additive compounds lies at the base of isomeric change in the oximes.

The behaviour of alkalis towards fused equimolecular mixtures of the oximes and dinitrochlorobenzene further emphasised the differences. In the case of the compounds with benz*anti*aldoxime and with *p*-methoxybenz*anti*aldoxime, treatment with cold 2*N*-sodium carbonate for a few hours brought about almost

quantitative conversion into the corresponding dinitrophenyl ethers, whilst 2*N*-sodium hydroxide acted much more rapidly. The mixture with *o*-methoxybenz*anti*aldoxime gave a small yield of dinitrophenyl ether with 2*N*-sodium hydroxide, but most of the oxime was recovered from the alkaline solution by the addition of ammonium chloride solution. The equimolecular mixture with *o*-hydroxybenz*anti*aldoxime gave no ether, the alkali dissolving the oxime and leaving the 2 : 4-dinitrochlorobenzene, a little of which was hydrolysed to dinitrophenol.

EXPERIMENTAL.

Action of 2 : 4-*Dinitrochlorobenzene on* anti-*Aldoximes.*—The reaction proceeds as follows :—

$$\begin{matrix} R\cdot CH \\ \| \\ HO\cdot N \end{matrix} \xrightarrow{NaOEt} \begin{matrix} R\cdot CH \\ \| \\ NaO\cdot N \end{matrix} \xrightarrow{(NO_2)_2C_6H_3Cl} \begin{matrix} R\cdot CH \\ \| \\ N\cdot O\cdot C_6H_3(NO_2)_2 \end{matrix}.$$

Equimolecular quantities of the *anti*-oxime and 2 : 4-dinitrochlorobenzene in warm alcoholic solution were treated with sodium (1 equiv.) dissolved in alcohol. A dark coloration immediately appeared followed after a few seconds by the precipitation of the ether. The solution was cooled, the solid separated, and washed with cold alcohol until free from dark colour and then with water to remove sodium chloride. The product was crystallised from boiling acetone, in which the dinitrophenyl ethers are sparingly soluble. The yield was usually about 80 per cent. of the calculated. The following 2 : 4-*dinitrophenyl ethers* were prepared in this way : of p-*methoxybenz*syn*aldoxime*, white needles, m. p. 174° (decomp.) (Found : N = 13·4. $C_{14}H_{11}O_6N_3$ requires N = 13·2 per cent.); of o-*aminobenz*syn*aldoxime*, brilliant sulphur-yellow, pleochroic needles, m. p. 177° (decomp.) (Found : N = 18·5. $C_{13}H_{10}O_5N_4$ requires N = 18·5 per cent.); of 5-*bromo*-3 : 4-*dimethoxybenz*syn-*aldoxime*, pale yellow needles, m. p. 199° (decomp.) (Found : N = 9·9. $C_{15}H_{12}O_7N_3Br$ requires N = 9·8 per cent.); of 3 : 4-*methylenedioxybenz*syn*aldoxime*, very pale yellow needles, m. p. 194° (decomp.) (Found : N = 12·7. $C_{14}H_9O_7N_3$ requires N = 12·7 per cent.); of o-*nitrobenz*syn*aldoxime*, white needles, m. p. 184° (decomp.) (Found : N = 17·2. $C_{13}H_8O_7N_4$ requires N = 16·9 per cent.); of p-*nitrobenz*syn*aldoxime*, white needles, m. p. 210° (decomp.) (Found : N = 16·5. $C_{13}H_8O_7N_4$ requires N = 16·9 per cent.); of p-*dimethylaminobenz*syn*aldoxime*, red needles, m. p. 185° (decomp.) (Found : N = 17·1. $C_{15}H_{14}O_5N_4$ requires N = 17·0 per cent.); of 3-*nitro*-p-*dimethylaminobenz*syn*aldoxime*, yellow needles, m. p. 179° (decomp.), which become bright red on exposure to light (Found : N = 18·5. $C_{15}H_{13}O_7N_5$ requires N = 18·6 per cent.).

In certain cases, the above general method was not so satisfactory. When applied to 3 : 4-dimethoxybenz*anti*aldoxime, only a 47 per cent. yield of the ether was obtained, but this was probably due to the somewhat greater solubility of the derivative in organic solvents; crystallised by dissolution in boiling acetone, addition of a little water, and cooling, the 2 : 4-*dinitrophenyl ether* of 3 : 4-*dimethoxybenz*syn*aldoxime* separated in pale yellow leaflets, m. p. 176° (decomp.) (Found : N = 12·4. $C_{15}H_{13}O_7N_3$ requires N = 12·1 per cent.). In the case of *o*-methoxybenz*anti*aldoxime the precipitated ether was contaminated with a considerable quantity of sodium dinitrophenoxide; this was removed by thorough washing with water, when the ether was obtained, but in only 34 per cent. yield. The 2 : 4-*dinitrophenyl ether* of o-*methoxybenz*syn*aldoxime* crystallised from acetone in white needles, m. p. 184° (decomp.) (Found: N = 12·9. $C_{14}H_{11}O_6N_3$ requires N = 13·2 per cent.). When 3-bromo-*p*-dimethylaminobenz*anti*aldoxime was treated in the usual way with 2 : 4-dinitrochlorobenzene and sodium ethoxide, no ether but only sodium dinitrophenoxide was obtained. The ether was, however, prepared by fusing together equimolecular quantities of the oxime and 2 : 4-dinitrochlorobenzene, cooling, and treating the finely powdered melt with cold 2*N*-sodium hydroxide. After some time the solid was separated, washed with water and then with acetone, to remove unchanged oxime and dinitrochlorobenzene, and the residue crystallised from boiling acetone, when the 2 : 4-*dinitrophenyl ether* of 3-*bromo*-p-*dimethylaminobenz*syn*aldoxime* was obtained in yellow needles, m. p. 181° (decomp.) (Found : N = 13·9. $C_{15}H_{13}O_5N_4Br$ requires N = 13·8 per cent.).

When *p*-hydroxybenz*anti*aldoxime was treated with equimolecular quantities of 2 : 4-dinitrochlorobenzene and sodium ethoxide, the *mono-dinitrophenyl ether* of p-*hydroxybenz*syn*aldoxime* was obtained which crystallised in white needles, m. p. 185° (decomp.) (Found: N = 14·2. $C_{13}H_9O_6N_3$ requires N = 13·9 per cent.). When two equivalents of dinitrochlorobenzene and sodium ethoxide were used, the same compound was obtained in better yield. A dinitrophenyl ether could not be prepared from *o*-hydroxybenz*anti*aldoxime either in alcoholic solution or by the action of dilute sodium hydroxide on the additive compound of the oxime and dinitrochlorobenzene (compare 3-bromo-*p*-dimethylaminobenz*anti*aldoxime above); the reaction invariably resulted in the decomposition of the dinitrochlorobenzene with the formation of sodium dinitrophenoxide.

Hydrolysis of the 2 : 4-*Dinitrophenyl Ethers.*—Four grams of the dinitrophenyl ether of *p*-methoxybenz*syn*aldoxime were heated under reflux on the water-bath for 4 hours with 150 c.c. of 6*N*-sodium

hydroxide, a strong odour of ammonia being observed. From the cooled solution after 12 hours sodium dinitrophenoxide (yielding 1·8 grams of 2 : 4-dinitrophenol) crystallised. The filtrate gave no precipitate on saturation with carbon dioxide, indicating that no oxime was present, but on acidification with hydrochloric acid 2·5 grams of *p*-methoxybenzoic acid were obtained. In a similar manner, the dinitrophenyl ethers of benz*syn*aldoxime, *o*-methoxy- and 3 : 4-methylenedioxy-benz*syn*aldoximes were hydrolysed to the corresponding acids. *p*-Dimethylaminobenz*syn*aldoxime dinitrophenyl ether, when so treated, gave a very troublesome product, but if the heating lasted for only 5 minutes, an oil was obtained which solidified on cooling and was identified as *p*-dimethylaminobenzonitrile.

Purification of the acid precipitated in the preceding process is rendered difficult by the presence of a small quantity of an amorphous material produced by partial decomposition of dinitrophenol. Hydrolysis for a very short time with 5 per cent. alcoholic potassium hydroxide gives much better results.

A mixture of 1 gram of the 2 : 4-dinitrophenyl ether of *o*-nitrobenz*syn*aldoxime and 30 c.c. of 5 per cent. alcoholic potassium hydroxide was heated and shaken for about 1 minute, the clear bright yellow solution immediately cooled, the crystals of potassium dinitrophenoxide were removed, and the filtrate was diluted with five or six times its volume of water; on keeping, *o*-nitrobenzonitrile crystallised out. The corresponding nitriles have been thus obtained by the hydrolysis of the dinitrophenyl ethers of *o*-nitro-, *m*-nitro-, *p*-nitro-, 3 : 4-dimethoxy-, 5-bromo-3 : 4-dimethoxy-, 3-nitro-*p*-dimethylamino-, *p*-hydroxy-, *o*-amino-benz*syn*aldoximes, and of cinnam*syn*aldoxime. In some cases, it was necessary to extract the nitrile from the diluted alcoholic solution with ether. Cinnamonitrile was identified by hydrolysis to cinnamic acid, and *p*-hydroxybenzonitrile, another specimen not being available for comparison as in the other cases, was converted into *p*-hydroxybenzoic acid.

Action of 2 : 4-*Dinitrochlorobenzene on* syn*Aldoximes.*—To 9 grams of cinnam*syn*aldoxime, dissolved in 15 c.c. of warm absolute alcohol, a solution of 1·3 grams of sodium in 40 c.c. of absolute alcohol was added, followed by 12 grams of 2 : 4-dinitrochlorobenzene in 20 c.c. of warm absolute alcohol. A dark red coloration immediately appeared and a brown precipitate formed. The solid was separated and after extraction with boiling benzene, which removed a small quantity of soluble matter which could not be identified, 7 grams of sodium dinitrophenoxide were obtained. The alcoholic filtrate was distilled in steam, when cinnamaldehyde was obtained in

considerable quantity. In a similar manner benzaldehyde was obtained from benz*syn*aldoxime, *p*-methoxybenzaldehyde from *p*-methoxybenz*syn*aldoxime, and heptaldehyde from heptaldoxime. All these aldehydes were identified by conversion into semicarbazones; acetaldehyde, from acetaldoxime, was recognised by its odour.

Fusion Diagrams of Binary Mixtures of Oximes with 2 : 4-*Dinitrochlorobenzene.*—The freezing points were obtained from cooling curves, the apparatus used being the same as that employed by Harris and one of us (J., 1923, **123**, 494). A commercial sample of dinitrochlorobenzene was repeatedly crystallised from alcohol until the melting point was constant; the product so obtained melted at 51° and froze in bulk at 49·4°. Benz*anti*aldoxime was dissolved in ice-cold benzene, well-cooled light petroleum added slowly with thorough stirring, and the solution seeded with a crystal of the oxime as soon as a faint turbidity appeared; the product melted in a capillary tube at 34° and froze in bulk at 33·7°. *p*-Methoxybenz*anti*aldoxime was crystallised from benzene; it melted at 64° and froze in bulk at 62·0°. *p*-Methoxybenz*syn*aldoxime was crystallised from benzene and melted at 134°. *o*-Methoxybenz*anti*aldoxime was crystallised from alcohol; it melted at 92° and froze in bulk at 88·4°. *o*-Hydroxybenz*anti*aldoxime was crystallised in the same way as benz*anti*aldoxime; it melted at 57° and froze in bulk at 55°.

Benzantialdoxime.—The results obtained are given in Table I.

TABLE I.

Mol. % of oxime.	F. p.	Mol. % of oxime.	F. p.	Mol. % of oxime.	F. p.	Mol. % of oxime.	F. p.
0°	49·4°	45·2	32·1°	65·2	27·8°	83·8	21·4°
8·0	45·4	47·7	32·3	71·8	24·3	84·9	22·6
18·0	42·0	50·0	32·5	77·2	21·2	90·2	26·1
31·1	36·6	53·0	32·4	79·8	20·0	95·6	30·1
40·0	31·9	57·4	31·9	81·2	20·1	100	33·7

An intermediate branch appears on the curve (see Fig. 1), the summit lying at 32·5°, corresponding with the formation of a compound of equimolecular proportions of the two constituents. The compound was isolated by melting together equimolecular quantities of 2 : 4-dinitrochlorobenzene and benz*anti*aldoxime and crystallising the product by dissolving it in well-cooled benzene and adding well-cooled light petroleum; the compound separated in white needles, m. p. 32—33°. It decomposed when left overnight suspended in 2*N*-sodium hydroxide or 2*N*-sodium carbonate; the insoluble residue was the dinitrophenyl ether of benz*syn*aldoxime.

p-*Methoxybenz*antialdoxime.—The results obtained are given in Table II.

TABLE II.

Mol. % of oxime.	F. p.	Mol. % of oxime.	F. p.	Mol. % of oxime.	F. p.	Mol. % of oxime.	F. p.
0	49·4°	37·8	63·3°	55·9	64·0°	81·5	47·0°
7·5	45·9	50·0	64·2	57·8	63·9	82·8	46·8
11·9	44·4	52·0	64·1	61·4	63·4	84·1	47·7
14·9	49·0	53·0	64·1	76·9	52·1	89·2	53·1
25·3	57·4	54·7	64·0	78·1	49·6	93·9	58·0
						100	62·0

There is a very well marked intermediate branch (see Fig. 1), the summit of which lies at 64·2°, corresponding with the formation of a compound of equimolecular proportions of the two constituents. This compound was isolated as in the preceding case, crystallised from benzene and light petroleum in yellow needles, m. p. 65°, and was decomposed by 2*N*-sodium carbonate, leaving a residue of the dinitrophenyl ether of *p*-methoxybenz*syn*aldoxime.

p-*Methoxybenz*syn*aldoxime.*—The results obtained are given in Table III.

TABLE III.

Mol. % of oxime ...	0	10·1	16·6	22·8	30·2	38·0	50·0
F. p.	49·4°	45°	47·3°	53·3°	57·7°	60·7°	63·0°

The curve (see Fig. 1) follows very closely the corresponding curve for the *anti*-oxime; the compound obtained by fusing together equimolecular quantities of the *syn*-oxime and 2 : 4-dinitrochlorobenzene was found, after crystallisation, to be identical with that formed from the *anti*-oxime, melting at 65° alone and when mixed with the latter substance.

o-*Methoxybenz*anti*aldoxime.*—The results are given in Table IV.

TABLE IV.

Mol. % of oxime.	F. p.	Eutectic.	Mol. % of oxime.	F. p.	Eutectic.	Mol. % of oxime.	F. p.
0	49·4°		37·0	37·4°		55·7	55·2°
10·9	44·8		39·0	37·9	37·4°	59·3	58·4
22·4	40·1	37·1°	41·5	39·7	37·2	64·2	64·1
28·0	36·8		45·0	45·0	37·4	72·0	69·1
32·0	37·3		47·6	47·4	36·7	79·4	75·6
34·0	37·5	36·6	50	49·0	37·0	88·3	82·1
34·5	37·6		53·6	51·9		95·3	85·8
						100	88·4

There is no indication (see Fig. 3) of a compound of equimolecular quantities of the two constituents, though there is some evidence of the formation of an unstable compound of dinitrochlorobenzene (2 mols.) and *o*-methoxybenz*anti*aldoxime (1 mol.). The product obtained by fusing together equimolecular quantities of the two compounds has been examined. Crystallisation from benzene gave o-methoxybenz*anti*aldoxime; treatment with 2*N*-sodium hydroxide in the cold converted the mixture partly into the dinitrophenyl

ether of *o*-methoxybenz*syn*aldoxime, which could be filtered off and purified; the alkaline solution, however, on the addition of a saturated solution of ammonium chloride gave a precipitate of *o*-methoxybenz*anti*aldoxime.

o-*Hydroxybenz*anti*aldoxime*.—The results are given in Table V.

TABLE V.

Mol. % of oxime.	F. p.	Mol. % of oxime.	F. p.	Mol. % of oxime.	F. p.
0	49·4°	43·6	(24·1°) 28·1°	69·7	30·4°
8·8	44·5	46·6	(21·2) 29·3	80·1	41·5
19·9	39·2	50·6	(17·6) 29·5	89·9	47·9
28·8	34·1	53·1	(11·7) 27·8	100	55·0
36·9	28·8	59·5	(18·8) 28·4		

A well-marked summit was observed (Fig. 2) corresponding with a temperature of 29·5° and equimolecular quantities of the constituents. This compound is characterised by the extreme slowness with which it crystallises, and owing to this it was possible to realise the whole of the first and third branches of the freezing-point curve below the eutectic temperatures of the compound (these results are given in brackets in Table V) by seeding with either 2 : 4-dinitrochlorobenzene or *o*-hydroxybenz*anti*aldoxime. Indeed points on the intermediate mound could be obtained only by seeding with a crystal of the compound, which first appeared from a considerably supercooled mixture of equimolecular quantities of the two components. These points are probably low, owing to unavoidable supercooling and the slow rate of crystallisation of the compound. This probably explains the fact that the longer part of the intermediate branch past the summit is on the side of the less fusible constituent. When equimolecular quantities of the components were fused and seeded with the compound, a hard, yellow, crystalline mass was obtained which melted at 32—33° but could not be recrystallised owing to dissociation into its components in solution. On treatment with 2*N*-sodium hydroxide or 2*N*-sodium carbonate the compound dissociated into its components, which reacted separately. The solid residue obtained consisted of sodium dinitrophenoxide and 2 : 4-dinitrochlorobenzene, whilst the alkaline solution, after acidification, gave on extraction with ether *o*-hydroxybenz*anti*aldoxime. Warming the compound with dimethylaniline and subsequent removal of the base with dilute hydrochloric acid gave a residue of dinitrochlorobenzene, whilst the oxime was recovered by extracting the acid solution with ether. In no case was there any indication of the formation of a dinitrophenyl ether.

THE RALPH FORSTER LABORATORY OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, February 14th*, 1924.]

CXXVIII.—*The Chlorination of Ethyl Alcohol.*

By Frederick Daniel Chattaway and Otto Guido Backeberg.

The interaction of two such familiar substances as chlorine and ethyl alcohol has naturally attracted the attention of many chemists (Liebig, *Annalen*, 1832, **1**, 182; Lieben, *ibid.*, 1857, **104**, 114; *Ber.*, 1870, **3**, 907; Personne, *Compt. rend.*, 1869, **69**, 1363; Fritsch, *Annalen*, 1894, **279**, 288), but the complete course of the reactions, which result ultimately in the formation of chloral, has never been satisfactorily settled.

With the intention of making more clear the initial stage of the reaction, the chlorination of alcohol has again been studied. It has been shown that ethyl hypochlorite and hydrogen chloride are first produced, and that acetaldehyde is formed from the hypochlorite by the elimination of hydrogen chloride.

As only an inconsiderable amount of ethyl chloride is formed at this stage, it is probable that the ethyl chloride recognised by Liebig and others is mainly produced by the slow interaction of the hydrogen chloride first formed with the alcohol present in excess.

The course of the reactions which lead to the formation of chloral alcoholate appears to be explained satisfactorily as follows.

When chlorine first acts on alcohol ethyl hypochlorite and hydrogen chloride are produced, the yellow colour of the solution being due to the hypochlorite. In the presence of excess of unchanged alcohol the ethyl hypochlorite very quickly breaks down into acetaldehyde and hydrogen chloride :

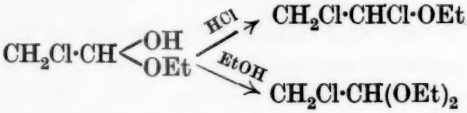
$$CH_3{\cdot}CH_2{\cdot}OH + Cl_2 \longrightarrow CH_3{\cdot}CH_2{\cdot}OCl + HCl.$$
$$CH_3{\cdot}CH_2{\cdot}OCl \longrightarrow CH_3{\cdot}CHO + HCl.$$

Under the influence of the hydrogen chloride present, the aldehyde is polymerised to paracetaldehyde. This is next chlorinated to *s*-trichloroparacetaldehyde, which to a small extent depolymerises under the influence of hydrogen chloride to monochloroacetaldehyde. This, immediately it is set free, combines with some of the still unattacked alcohol to form monochloroacetaldehyde alcoholate.*

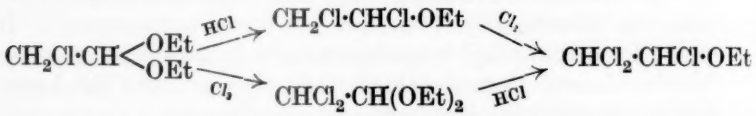
$$CH_3{\cdot}CHO \xrightarrow{HCl} (CH_3{\cdot}CHO)_3 \xrightarrow{Cl_2} (CH_2Cl{\cdot}CHO)_3 \xrightarrow{HCl}$$
$$CH_2Cl{\cdot}CHO \xrightarrow{EtOH} CH_2Cl{\cdot}CH(OH){\cdot}OEt.$$

* Natterer (*Monatsh.*, 1884, **5**, 497) found that when monochloroacetaldehyde is added to alcohol heat is evolved and monochloroacetaldehyde alcoholate is formed.

This compound now reacts both with alcohol, which is still present, to form monochloroacetal, and with hydrogen chloride, which has now been produced in considerable amount, to form dichloroethyl ether.



Further chlorination of each of these compounds leads to the formation of trichloroethyl ether, chlorination of monochloroacetal occurring either before or after its conversion into a chloro-ether by the hydrogen chloride, now present in great excess :



At this stage the liquid separates into an upper layer, consisting chiefly of a saturated solution of hydrogen chloride in water, and a lower layer of trichloroethyl ether. On warming, the two layers disappear and the liquid again becomes homogeneous, the trichloro-ether reacting with the water of the upper layer and forming dichloroacetaldehyde alcoholate :

$$CHCl_2{\cdot}CHCl{\cdot}OEt + H_2O \longrightarrow CHCl_2{\cdot}CH(OH){\cdot}OEt + HCl.$$

The dichloroaldehyde alcoholate is then very slowly chlorinated to chloral alcoholate, which is the final product of the reaction, the hydrogen chloride escaping at the high temperature which is required during the last stage of the chlorination.

Experimental.

Action of Ethyl Hypochlorite upon Alcohol.—Ethyl hypochlorite (usually 12—13 grams, prepared from 10 grams of alcohol and 20 grams of sodium hydroxide in 100 c.c. of water by the method previously described [*J.*, 1923, **123**, 3000]) was run as rapidly as possible through a tap-funnel into 20 c.c. of alcohol contained in a half-litre flask. This was cooled by ice and fitted with a double-walled condenser which was connected to a Volhard trap containing alcohol, similarly cooled, to retain any volatile products which might escape condensation. Within a minute a very vigorous reaction occurred accompanied by the evolution of heat and sometimes by a crackling sound. This action soon ceased and a colourless liquid containing much free hydrogen chloride remained in the flask. This and the contents of the Volhard trap were without

delay poured into a flask containing an excess of precipitated calcium carbonate. It was found impracticable owing to the energetic action to bring more than these comparatively small quantities together at a time.

The operations were repeated until about 230 grams of ethyl hypochlorite had been added to 370 c.c. of alcohol. The whole was then filtered from the excess of calcium carbonate and distilled, when a considerable quantity of acetaldehyde came over; the bulk, however, was found in the residue, where it had been converted into paracetaldehyde and acetal.

Identification of Ethyl Hypochlorite as the First Product of the Chlorination of Alcohol.—Dry chlorine was passed through a fine tube, very slowly to avoid heating, into 5 c.c. of alcohol cooled to −18°. A yellow liquid was obtained which appeared identical with a freshly made, cold, dilute alcoholic solution of ethyl hypochlorite. Both had the same characteristic odour and both liberated iodine at once when added to a slightly acidified solution of potassium iodide. Both lost their yellow colour at the ordinary temperature, in a short time when light was excluded, and much more rapidly in bright light. In both cases hydrogen chloride was freely evolved during the decoloration and the presence of acetaldehyde in considerable quantity could be recognised in the acid colourless product. In view of the vigorous and immediate decomposition of ethyl hypochlorite in presence of alcohol, it was necessary, if it was to be identified, to chlorinate in an apparatus in which the bulk of the alcohol reacted almost immediately, and in which heating was avoided as far as possible. This was done by allowing small drops of alcohol distributed over a large, cooled surface to meet an excess of chlorine. Dry alcohol was allowed to drop slowly from a tap funnel drawn out to a fine capillary, down a narrow, cooled tube packed with glass beads up which a stream of chlorine was passed. Light was carefully excluded. The liquid product which condensed in the tube was collected in a well-cooled, blackened flask. Owing to the heat unavoidably produced locally, a small proportion of the products distilled over; this was condensed and collected in a similar cooled, blackened flask attached to the exit tube.

The stream of chlorine passing through the apparatus was so regulated that some of it issued unchanged from the exit tube. It was found that the alcohol could not be admitted faster than about 1 c.c. a minute, this rate allowing the heat produced to be dissipated. If the tube was not sufficiently cooled or if the alcohol was allowed to enter more rapidly, decomposition accompanied by a yellow flame occurred and carbon was deposited. Most of the reaction

took place on the upper layer of beads, and the tube became slightly warm at that point. The product obtained was a heavy, yellow, fuming liquid with the irritating, characteristic odour of ethyl hypochlorite. It was poured on to crushed ice, when a yellow oil containing ethyl hypochlorite with some more highly chlorinated products separated as a lower layer. This was rapidly washed with iced water, separated, and dried over fused calcium chloride. To estimate the amount of ethyl hypochlorite present, a small, weighed portion was added to a solution of potassium iodide acidified with acetic acid, and the liberated iodine titrated. The amount was found to vary with the conditions and duration of the experiment. Collected as described above, in one experiment 8·2 per cent. of ethyl hypochlorite was found to be present. In a second experiment, in which the separation and drying were carried out more rapidly, 12·9 per cent. of ethyl hypochlorite was found to be present in the oil separating from the liquid condensed in the tube and 10·2 per cent. in the oil separating from the liquid which distilled over and condensed in the flask attached to the exit tube. It was found impracticable to obtain the ethyl hypochlorite in a pure condition by distillation. On heating the yellow oil rapidly, it boiled vigorously with obvious decomposition at about 40°, much hydrogen chloride was liberated, and a small quantity of a yellow liquid distilled over which contained only about 6 per cent. of ethyl hypochlorite.

Complete Chlorination of Alcohol without Cooling or External Heating.—A litre of 97 per cent. alcohol was allowed to drop through a capillary down the tube packed with beads previously described at the rate of about 1 c.c. in 5 minutes. Neither the tube nor the collecting flask was cooled, and a sufficient current of chlorine was maintained for it to escape freely from the exit. The alcohol was thus subjected to the action of excess of chlorine for a considerable period at a temperature not far removed from the ordinary. 998 Grams of a nearly colourless, fuming liquid, separated into two layers, collected in the receiver. The upper layer ($d_{4^\circ}^{16^\circ}$ 1·11), which consisted largely of water, weighed 582 grams and the lower layer ($d_{4^\circ}^{16^\circ}$ 2·22) weighed 416 grams. To the mixed layers a saturated solution of potassium carbonate was added until the free hydrochloric acid was neutralised. The liquid now separated into two layers, a lower layer consisting of a strong solution of potassium chloride and an upper, oily layer of a pale yellow colour giving off vapours which had a very irritating effect on the eyes. The pale yellow, oily liquid ($d_{4^\circ}^{16^\circ}$ 1·2) weighed 433 grams. It could not be separated into its constituents by fractionation. On heating, a considerable amount distilled over in the neighbourhood of 92°;

the temperature then rose rapidly to about 150°, when almost complete decomposition and charring of the remainder, a large part of the whole, occurred. The liquid distilling in the neighbourhood of 92°, which appeared to be a mixture of impure monochloroacetaldehyde alcoholate with some di- and tri-chloroether and a small quantity of monochloroacetaldehyde, could not itself be separated into its constituents, as on refractionation it decomposed with much frothing. As no pure product could be isolated by fractionally distilling the oily product, either under the ordinary or reduced pressure, a further quantity, prepared as above, was added to an equal weight of alcohol together with an excess of powdered chalk and the mixture heated to boiling for 8 hours. The product was then filtered and poured into water, when an oily liquid separated as a lower layer. This was washed with a little water, dried over calcium chloride, and fractionally distilled. It was thus separated into two main fractions boiling constantly at 155° and 182°, respectively, which analysis showed to be monochloroacetal (Found : Cl = 23·77. Calc., Cl = 23·24 per cent.), and dichloroacetal (Found : Cl = 38·11. Calc., Cl = 37·92 per cent.).

THE QUEEN'S COLLEGE, OXFORD. [*Received, January 29th,* 1924.]

CXXIX.—*The Effect of Complex Formation on Oxidation Potentials. The Influence of the Cyanide-ion on the Ferrocyanide–Ferricyanide Potential.*

By J. A. V. BUTLER and GEORGE PARKER DAVIES.

IT is a well known fact that the oxidising and the reducing properties of metallic ions are greatly modified when they enter into complexes. This effect has usually been referred to the reduction in the concentrations of " free " ions in the presence of the complex-forming substance according to the equilibrium constants of the complexes.

This view assumes that the " free " ions alone are electromotively active. Without entering into the controversy (Haber and others, *Z. Elektrochem.*, 1904) as to the reality of the minute ionic concentrations to which this theory leads, two cogent reasons may be adduced for believing that the complex ions themselves are electromotively active : (1) the ease and velocity of many oxidation and reduction processes in which complex ions are concerned, (2) the fact that the " free " ions themselves are almost certainly present in aqueous solution in the form of hydrate complexes, and there

are no grounds for postulating electrochemical behaviour radically different for complexes of different types.

If we adopt the view that a complex ion can be directly oxidised or reduced, that is, may increase or decrease its total ionic charge without disturbance to the associated molecules, it becomes a matter of interest to determine the effect on the oxidation potential of the replacement of the inner sheath of water molecules attached to the "free" ion by molecules of other kinds.

Some data of this kind of course exist, but before studying the general question from this point of view it is necessary to know how far the oxidation potential depends on the amount of the complex-forming substance in solution.

Consider two ions M_1 and M_2 of the same metal with n_1 and n_2 positive charges respectively, which combine with p_1 and p_2 molecules of the species C forming the complex ions ($M_1C_{p_1}$) and ($M_2C_{p_2}$). The oxidation of ($M_1C_{p_1}$) to ($M_2C_{p_2}$) may be expressed by the equation

$$M_1C_{p_1} + (p_2 - p_1)C = M_2C_{p_2} + (n_2 - n_1)\epsilon.$$

If the law of mass action holds, the following equation for the oxidation potential may be obtained thermodynamically independent of any particular mechanism,

$$E = E_0 + \frac{RT}{(n_2 - n_1)F} \log_e \frac{[MC_{p_2}]}{[M_1C_{p_1}][C]^{p_2 - p_1}} \quad . \quad . \quad (1)$$

where the concentrations are expressed in square brackets and E_0 is the normal potential.

It will be seen that if the oxidation involves a change in the number of molecules associated with the metallic ion, the oxidation potential must depend on the concentration of the complex-forming substance.

But if the complex ions concerned differ only in the total ionic charge, that is, $p_1 = p_2$, the oxidation potential is independent of the concentration [C], provided that the amounts of the complex ions in solution are not appreciably affected.

It was our object in the first place to test this deduction. The most suitable substances for the purpose appeared to be the complex cyanides of iron. The stability of the ferrocyanide- and ferricyanide-ions ensures that on adding further amounts of the cyanide-ion no appreciable change in the concentrations of the complex ions will occur. Further, the oxidation potentials of this system have been extensively studied (Fredenhagen, *Z. anorg. Chem.*, 1902, **29**, 396; Schaum and Linde, *Z. Elektrochem.*, 1903, **9**, 407; Schoch, *J. Amer. Chem. Soc.*, 1904, **26**, 1422; Lewis and Sargent, *J. Amer. Chem. Soc.*, 1909, **31**, 355; Müller, *Z. physikal. Chem.*, 1914, **88**, 46). The potentials of mixtures of potassium ferro- and

ferri-cyanides in the same proportions have been found to vary with the total concentration. Schoch and Felsing (*J. Amer. Chem. Soc.*, 1916, **38**, 1928) have shown that the observed potential is a function of the potassium-ion concentration in the mixture. They also investigated the effect of additions of potassium chloride and showed that the effect was to be ascribed entirely to the potassium-ion.

If, therefore, the oxidation potentials of a series of ferro-ferricyanide mixtures with various additions of potassium cyanide be determined, the effect of the cyanide-ion on the potential will be obtained after allowing for the effect of the potassium-ion.

The actual mixtures with potassium chloride used by Schoch and Felsing were not quite suitable for the comparison. Parallel measurements were therefore made in which the concentrations of ferrocyanide and ferricyanide of potassium were the same and equivalent amounts of the chloride and cyanide were added. Correcting for small differences in the degrees of ionisation of the chlorides and cyanides of potassium, we should therefore obtain the effect of the cyanide-ion itself.

Experimental.

The potentials of ferro-ferricyanide mixtures in the presence of potassium cyanide varied rapidly with the time, owing to the rapid disappearance of the ferricyanide. In fairly concentrated solutions of potassium cyanide the mixture rapidly darkened and eventually became black. The main reaction appeared to be the oxidation of cyanide to cyanate by the ferricyanide. Evidently this was accompanied by condensations giving a deep colour.

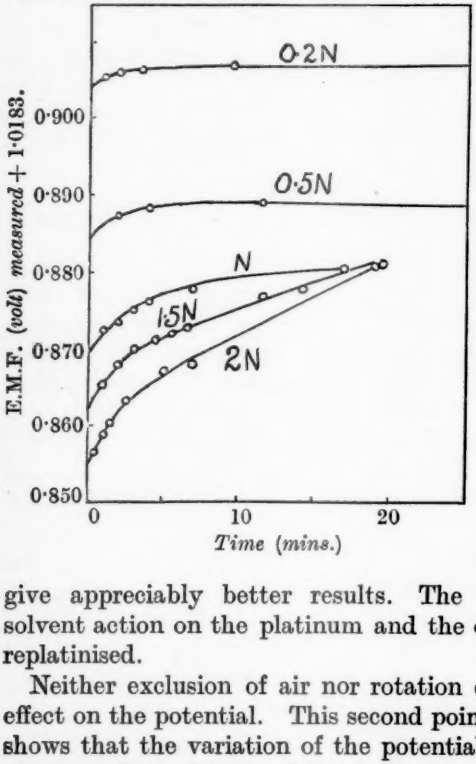
The rate of change could be very greatly reduced by working with a solution in which the proportion of ferrocyanide to ferricyanide was large (10 : 1). In such solutions the rate of change of the potential was comparatively small and could easily be observed. One of the characteristic features of the ferro-ferricyanide potential is the fact that has frequently been observed (Lewis and Sargent, *loc. cit.*) that the electrode potential is taken up almost instantaneously. The true potentials of such mixtures can therefore be determined by extrapolating the potential measurements back to the time of mixing. Fig. 1 illustrates this procedure for one series of our measurements.

It was recognised that in these circumstances this system could scarcely be expected to give an exact test of the relation, but no system is available in which the conditions are so well-known and unambiguous. It therefore seemed to be worth while to continue the investigation.

The solutions were made up by rapidly mixing measured quantities of stock solutions (potassium cyanide last) at the temperature of the thermostat and diluting to the required volume. The mixture was introduced into the electrode vessel as quickly as possible and usually the first reading could be taken within a minute of mixing.

The potentials were measured against a carefully prepared normal calomel electrode, which was checked at intervals against a second with which it agreed throughout. The calomels were at room temperature, which was frequently observed by a thermometer in the liquid and the appropriate correction applied. The electrode vessel was kept in a thermostat at 25° ± 0·1°.

FIG. 1.
Variation of E.M.F. *with time. Series III (a).*



Two electrodes of platinised platinum were employed in each experiment, but owing to the quick succession of the initial readings, only one was observed, the other being used as a check at a later stage. Other investigators have recommended the use of gold-plated electrodes. We found that gold platings quickly dissolved in the cyanide solutions. We also tried iridised electrodes, but they did not give appreciably better results. The cyanide exerted a slight solvent action on the platinum and the electrodes were frequently replatinised.

Neither exclusion of air nor rotation of the electrodes had any effect on the potential. This second point is of interest, because it shows that the variation of the potential is not due to changes in the immediate vicinity of the electrodes.

The *E.M.F.*'s were measured by a Tinsley ionisation potentiometer, which gave readings directly to 1 millivolt and by estimation to about 0·2 millivolt, in conjunction with a standard Weston cell.

Three series of measurements were made at the concentrations stated. The initial values for the *E.M.F.*'s obtained by extra-

polation to the time of mixing from the experimental readings, and corrected to 25° are given in Table I.

TABLE I.

E.M.F.'s of Cells at 25°.

	Series I. $K_4Fe(CN)_6$ 0·04*M*. $K_3Fe(CN)_6$ 0·004*M*.		Series II. $K_4Fe(CN)_6$ 0·02*M*. $K_3Fe(CN)_6$ 0·002*M*.		Series III. $K_4Fe(CN)_6$ 0·01*M*. $K_3Fe(CN)_6$ 0·001*M*.	
	(*a*).	(*b*).	(*a*).	(*b*).	(*a*).	(*b*).
x.	KCN,*x*M.	KCl,*x*M.	KCN,*x*M.	KCl,*x*M.	KCN,*x*M.	KCl,*x*M.
0	0·0865	0·0865	0·073	0·073	0·065	0·065
0·01	0·087	0·087	0·075	0·0765	0·0675	0·069
0·02	0·088	0·088	0·078	0·079	0·069	0·072
0·04	0·091	0·0905	0·082	0·083	0·076	0·077
0·1	0·097	0·0965	0·090	0·090	0·089	0·0875
0·2	0·105	0·1045	0·100	0·995	0·098	0·099
0·5	0·121	0·1195	0·119	0·117	0·117	0·1175
1·0	0·134	0·135	0·133	0·133	0·131	0·1335
1·5	0·1435	0·1455	—	0·145	0·140	0·1455
2·0	0·151	0·156	0·147	0·154	0·149	0·1535

Discussion.

In view of the rapid change of the cyanide mixtures we did not expect to obtain more than an approximation to the effect of the cyanide-ion on the potential. In the more dilute solutions, the effects of additions of potassium cyanide are, within the experimental error, the same as those of equivalent amounts of potassium chloride. In the most concentrated solutions, there are differences of several millivolts. These differences cannot be ascribed to differences in the degrees of dissociation of potassium chloride and cyanide. The conductivity data for strong solutions of potassium cyanide are very meagre, but it appears from two determinations of Kohlrausch (Kohlrausch and Holborn, " Das Leitvermögen der Elektrolyte ") that the degree of dissociation of 2*N*-potassium cyanide is somewhat greater than that of 2*N*-potassium chloride. The actual divergence is the reverse of that which would be expected on this account. It can only be concluded that the effect of the cyanide-ion on the potential is small and amounts at most to a few millivolts in 2*N*-potassium cyanide.

The Potential of Iron in Ferrocyanide Solutions.

With the hope of accounting for the curious and somewhat contradictory results obtained by early workers on the potential of iron in ferrocyanide solutions, and of determining the " apparent concentration " of ferrous-ions in equilibrium with ferrocyanide, we have carried out numerous experiments on this potential. The effect of many factors has been studied, for example different

methods of preparation of the iron electrode, the effect of stirring, exclusion of air, additions of potassium cyanide, etc. We persistently obtained potentials in which the iron was more positive in solutions of potassium ferrocyanide than in a dilute solution of a ferrous salt (that is, the tendency to dissolve in the ferrocyanide was less than in a solution in which the ferrous-ion concentration was enormously greater). The potentials, however, were very greatly dependent on the mode of preparation of the electrode, etc., and we were unable to obtain any reproducible potential which could be regarded as having any thermodynamical significance.

In conclusion, we desire to express our appreciation of the facilities afforded us in the course of this work by Prof. J. E. Coates, D.Sc., O.B.E. One of us (G.P.D.) was enabled to collaborate in this work by the award of a Research Studentship of the University of Wales, for which he desires to express his thanks.

UNIVERSITY COLLEGE OF SWANSEA. [*Received, January 29th*, 1924.]

CXXX.—*The Hydroferrocyanides and Hydroferricyanides of the Organic Bases. Part III.*

By WILLIAM MURDOCH CUMMING.

SEVERAL new hydroferrocyanides, precipitated in alcoholic solution, have been prepared; these have properties similar to those already described (J., 1922, **121**, 1287; 1923, **123**, 2457). The compositions were ascertained by estimation of the iron and, if necessary, of the nitrogen also. The formulæ, etc., are given in the following table, the same symbols being used as before, *C* representing C_2H_6O.

Base.	Formula.	Crystalline structure, etc.
*iso*Quinoline	A_2,B	Lemon-yellow, rhombohedral. s.
o-Anisidine	$A_2,B,\frac{1}{2}C$	White prisms. s.
Benzylamine	A_4,B	White plates. s.
Piperazine	$A_2,B,2C$	White plates. s.
Piperidine	A_4,B,C	White, rhombic. s. ss.
2 : 4-Tolylenediamine	A_3,B,C	White, rhombohedral. s.
Tetramethyldiaminodiphenylmethane	$A_2,B,2C$	White prisms. s.
Dimethylaminoazobenzene	A,B,C	Crimson plates. s.
Hexamethylenetetramine .	$A_2,B,\frac{1}{2}C$	White plates. s.
o-Phenylenediamine	$A_4,B,5C$	White plates. s.
m- ,, ...	$A_4,B,4C$	White plates. s.
p- ,, ...	$A_4,B,2C$	White plates. s.

Hydroferricyanides of the Organic Bases.

The hydroferricyanides were produced from the hydrochloride of the base and potassium ferricyanide in acid or neutral solution,

the method being similar to that used in the preparation of the hydroferrocyanides; in dilute solutions crystallisation occurred sometimes only after several hours. The salts of primary amines could not be isolated owing to oxidation even in dilute solution at −20°; benzylamine, α-phenylethylamine, and *l*-menthylamine gave no oxidation products.

Most secondary amines gave pure salts only at low temperatures; diphenylamine and *p*-methylaminophenol underwent oxidation. No oxidation of tertiary amines took place at the ordinary temperature except in the cases of dimethylaminoazobenzene, tetramethyldiaminodiphenylmethane, and methyldiphenylamine. Pyridine, piperidine, and piperazine gave no salt in neutral solution, and trimethylamine hydroferricyanide could not be isolated.

Hydroferricyanides could not be prepared from bases containing an acid substituent in the nucleus, except in the cases of *p*-bromo- and *p*-nitroso-dimethylaniline. The presence of such a group in a primary amine prevented colour change and oxidation. With substances such as acetanilide, oxidation took place only after the compounds had been hydrolysed by continued boiling.

General Properties.—The hydroferricyanides are of definite crystalline form and are generally highly coloured, usually bright yellow. They are more stable and more highly coloured than the corresponding hydroferrocyanides. They are sparingly soluble in cold water, and usually insoluble in absolute alcohol or ether.

Hydroferricyanides of organic bases prepared in acid and in neutral solution [B = $H_3Fe(CN)_6$].

Base.	Acid solution.		Neutral solution.	
Monomethylaniline.	$A_3,B,\frac{1}{2}C$	Lemon-yellow prisms. s.	$A_3,B,\frac{1}{2}C$	Lemon-yellow prisms. s.
Dimethylaniline.	$A_2,B,3C$	Lemon-yellow, prismatic needles.	$A_2,B,3\frac{1}{2}C$	Lemon-yellow needles. s.
p-Nitrosodimethylaniline.	$A_2,B,3C$	Greenish-brown prisms. s.	A_3,B,C	Golden needles. s.
p-Bromodimethylaniline.	$A_2,B,3C$	Brown prisms.	$A_3,B,3C$	Green plates. s.
Pyridine.	$A_2,B,2C$	Yellow, rhombic. s. ss.		
Quinoline.	$A_3,B,2C$	Yellow, rhombohedral. s.	$A_3,B,3C$	Yellow plates. s.
*iso*Quinoline.	A_3,B,C	Yellow, rhombohedral. s. ss.	$A_3,B,3C$	Lemon needles. s.
Piperazine.	A,B,C	Brownish-yellow prisms. s. ss.		
Piperidine.	$A_2,B,2C$	Yellow, rhombic. s. ss.		
Hexamethylenetetramine.	$A_2,B,2C$	Yellow, cubic. s.	$A,B,7\frac{1}{2}C$	Orange, rhombic.
Benzidine.	A_3,B	Blue plates.	$A_3,B,3C$	Blue plates.

Benzidine hydroferricyanide hydrochloride, $A_4,B,2HCl$, precipitated in stable, bright green plates when a dilute potassium ferricyanide solution is added to benzidine dihydrochloride in dilute hydrochloric acid at −15°, blackens and fuses when heated, a white sublimate of benzidine dihydrochloride being formed (Found : Fe = 5·01; N = 17·58. Calc., Fe = 4·98; N = 17·43 per cent.). When treated with water, it yields a stable blue salt, infusible plates, which has the characteristic properties of the hydroferricyanides, and is insoluble in water or absolute alcohol (Found : Fe = 7·30. A_3,B requires Fe = 7·30 per cent.). When the blue salt is treated with dilute hydrochloric acid, in which it is fairly soluble, the green salt is regenerated (Found : Fe = 4·97 per cent.).

Cole (*Philippine J. Sci.*, 1923, **23**, 97), in an investigation of the use of potassium ferrocyanide as a reagent in the qualitative microanalysis of the common alkaloids, erroneously suggests the formula $(base)_2,H_4Fe(CN)_6,xH_2O$ for the salts precipitated in acid solution. The alkaloid salts were among the first prepared by the present author, and it was early recognised that microscopic examination would afford a means of identifying many alkaloids. The hydroferro- and hydroferri-cyanides of several alkaloids have been prepared in acid, neutral, and alcoholic solution and their constitutions determined. The author hopes to continue this investigation and to prepare microphotographs. It is desired therefore to reserve this field of work.

ROYAL TECHNICAL COLLEGE,
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CXXXI.—*Reduction of Nitronaphthalenes. Part II. Reduction of β-Nitronaphthalene.*

By WILLIAM MURDOCH CUMMING and GEORGE STRATON FERRIER.

ON reduction with zinc dust and alcoholic ammonium chloride (see Cumming and Steel, J., 1923, **123**, 2466), β-nitronaphthalene yields ββ′-azoxynaphthalene and ββ′-azonaphthalene. Further reduction to ββ′-hydrazonaphthalene undoubtedly occurs, but this compound undergoes atmospheric oxidation and the benzidine transformation with almost equal ease, and accordingly only ββ′-azonaphthalene or 2 : 2′-diamino-1 : 1′-dinaphthyl has been isolated from the reaction product.

ββ′-Azonaphthalene, unlike the αα′-isomeride (Cumming and Steel, *loc. cit.*), does not oxidise in air; it is, however, converted into ββ′-azoxynaphthalene by hydrogen peroxide in glacial acetic acid solution.

ββ′-Azoxynaphthalene, which has a pure yellow colour and melts at 164°, on exposure to light, preferably in alcoholic solution, is converted into a red isomeride melting at 162°. The change is irreversible and both forms are stable towards alcohol in the dark. Knipscheer (*Rec. trav. chim.*, 1903, **22**, 1) has shown that azoxybenzene is converted by the action of light into *o*-hydroxyazobenzene, and a similar change of αα′-azoxynaphthalene was noted by Baudisch and Fürst (*Ber.*, 1912, **45**, 3426); Cumming and Steel (*loc. cit.*) found that their two compounds had identical melting points and suggested that they were structural isomerides.

Attempts to characterise our red modification as a hydroxyazonaphthalene by benzoylation and by methylation failed, but support for this view is afforded by a comparison of the absorption spectra of both forms with that of β-naphthaleneazo-β-naphthol (no unsubstituted hydroxy-2 : 2′-azonaphthalene appears to have been prepared). It will be seen (Fig. 1) that the red substance (m. p. 162°) and β-naphthaleneazo-β-naphthol both produce a band with its head at a frequency approximately 1950 units which is not shown by ββ′-azoxynaphthalene, and that the characteristic absorption bands of ββ′-azoxynaphthalene are not shown by the red substance.

The properties of 2 : 2′-diamino-1 : 1′-dinaphthyl and the action of light on azoxy-compounds are being investigated.

Experimental.

β-Nitronaphthalene was prepared by Meisenheimer and Witt's method (*Ber.*, 1903, **36**, 4153) and extracted from the reaction product with alcohol. If purified simply by crystallisation, it forms yellow or yellowish-red needles (as stated in the literature), but after contact with animal charcoal in boiling alcoholic solution it can be obtained almost colourless; the melting point (79°) is unaltered by this treatment.

Preparation of ββ′-Azoxynaphthalene.—1. *By reduction of β-nitronaphthalene.* The reduction was carried out by Cumming and Steel's method (*loc. cit.*), and when all the zinc dust had been added the hot reaction mixture was filtered and the residue and the filtrate (A) were worked up separately. The residue was extracted with alcohol, with hot water, and again several times with alcohol. The first alcoholic extract yielded only a small quantity of white plates melting or decomposing at 220—230°. The remaining alcoholic extracts on concentration and cooling yielded ββ′-azoxynaphthalene. The filtrate (A) deposited a crystalline mass, and more was obtained by concentrating the mother-liquor. This product was extracted with water and then exhaust-

ively with alcohol, the residue being a white powder containing zinc (compare Cumming and Steel, *loc. cit.*). The alcoholic extracts on concentration and cooling yielded ββ′-azoxynaphthalene.

After several crystallisations from alcohol the azoxynaphthalene was obtained in yellow needles, m. p. 164° (Meisenheimer and Witt give m. p. 167—168°) (Found: N = 9·25. Calc., N = 9·39 per cent.).

2. *By oxidation of* ββ′*-azonaphthalene.* Five grams of ββ′-azonaphthalene, prepared by Hantzsch and Schmeidel's method (*Ber.*, 1897, **30**, 81), were heated with a litre of glacial acetic acid and 80 c.c. of perhydrol on the water-bath in the dark for 6—8 hours. The cooled, filtered solution, now yellow in colour, was concentrated, a few drops of water were added, and the bulky, reddish-yellow product thereby obtained was treated with animal charcoal in boiling alcohol, ββ′-azoxynaphthalene, m. p. 164°, crystallising on cooling.

Action of Light on ββ′*-Azoxynaphthalene.*—A 0·1 per cent. alcoholic solution of ββ′-azoxynaphthalene on exposure to sunlight or to the rays of a mercury vapour lamp rapidly changed in colour from pale yellow to deep red and on concentration yielded red crystals, m. p. 162°; a mixture of these with ββ′-azoxynaphthalene melted at 157—159°.

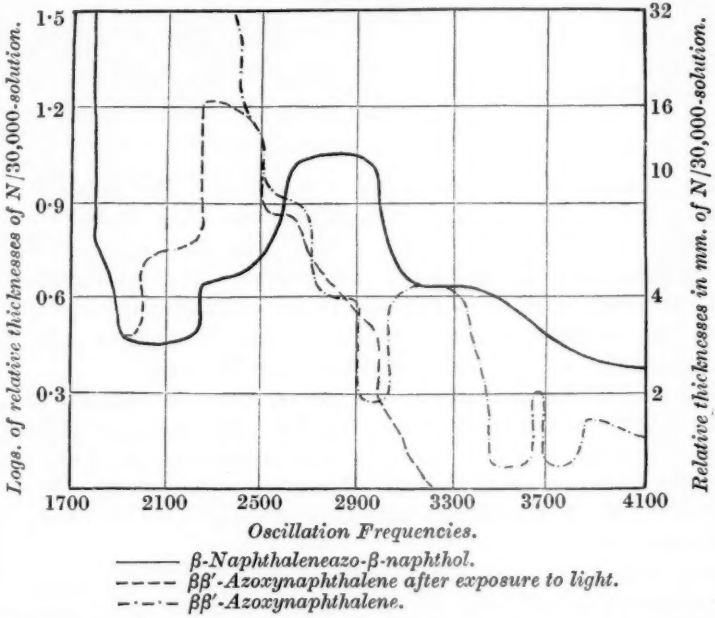
The red product was slightly soluble in sodium hydroxide solution and was reprecipitated by hydrochloric acid. Treated with benzoyl chloride and aqueous sodium hydroxide, it gave a blood-red solution, from which a yellow oil separated; this crystallised on cooling and scratching and proved to be yellow ββ′-azoxynaphthalene (Found: N = 9·36 per cent.). A mixture of 0·5 gram of the red modification, 25 c.c. of 30 per cent. aqueous sodium hydroxide, and 10 c.c. of methyl sulphate was well shaken and then heated for 5 minutes; the red oil that ultimately separated and solidified proved to be a mixture of the initial material with a small quantity of yellow ββ′-azoxynaphthalene.

A *N*/3000-solution of ββ′-azoxynaphthalene was divided into two portions, one of which was kept in the dark while the other was exposed to the light of the mercury vapour lamp for 8 hours. The absorption spectra of both solutions and also, for comparison, of a solution of β-naphthaleneazo-β-naphthol (Nietzki and Goll, *Ber.*, 1886, **19**, 1282) were then photographed at *N*/30,000-dilution (Fig. 1).

ββ′*-Azonaphthalene.*—The reduction of β-nitronaphthalene was carried out as above, zinc dust being added until the colour of the solution was completely discharged. The reaction mixture was filtered hot and the residue washed several times with hot alcohol. The united alcoholic filtrates, which rapidly reddened on exposure to air, were allowed to cool and filtered. On crystal-

lising the product from alcohol, orange-yellow needles, m. p. 204°, were obtained which were identified as ββ′-azonaphthalene by comparison with a sample prepared by Hantzsch and Schmiedel's method (*loc. cit.*). On evaporating the mother-liquor, two crops of yellowish-red crystals, m. p. 157—158°, were obtained. These crystals were to all appearances identical with the crude product of the oxidation of ββ′-azonaphthalene with hydrogen peroxide, but the quantity obtained was too small for further examination.

FIG. 1.



2 : 2′-*Diamino*-1 : 1′-*dinaphthyl*.—With the object of isolating ββ′-hydrazonaphthalene, β-nitronaphthalene was reduced as before and the reaction mixture was immediately concentrated under reduced pressure in order to prevent atmospheric oxidation. A copious yield of white plates was obtained which, however, after crystallisation melted at 189—191°, and resembled in their properties 2 : 2′-diamino-1 : 1′-dinaphthyl (Meisenheimer and Witt, *loc. cit.*).

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CXXXII.—*The Hydrogen Overvoltage of Zinc.*

By GEORGE MEREDYTH WESTRIP.

TAFEL (*Z. physikal. Chem.*, 1905, **50**, 641) made an important investigation of the phenomena of hydrogen overvoltage, using the so-called direct method of measurement. A notable omission in that work, however, was a study of the zinc cathode. The importance of such data in connexion with the electrolytic deposition of zinc is sufficient to warrant an investigation using the direct method of measurement.

The object of this research was to obtain data concerning the hydrogen overvoltage of zinc at high current densities, and to study the effect of various impurities in the electrolyte upon it.

EXPERIMENTAL.

The electrolytic cell was a 900 c.c. beaker. The anode was a ring of lead, 7·5 cm. in diameter and 2·5 cm. wide, coated electrolytically with lead peroxide before use. The zinc cathode, 1·5 cm. in diameter and 13 cm. long, was cast out of pure electrolytic zinc, in a mould made of asbestos paper embedded in silver sand. With the exception of an annular portion of definite area, the surface of the cathode was coated with paraffin wax.

The current for electrolysis was drawn from the lighting mains, and could be varied from 0·01—4·0 amps. The reference electrode was a hydrogen electrode made up with sulphuric acid of the same strength as that used in the cell. A calibrated bridge wire, Weston standard cell, and capillary electrometer were used for measuring potential difference.

The end of the syphon connecting the hydrogen electrode with the electrolytic cell was drawn out into a thin-walled capillary 0·3 mm. in internal diameter, which was bent upward at an angle of about 30° to the horizontal and pressed almost tangentially against the cathode surface. During a series of measurements a continuous flow of electrolyte was maintained through the capillary from a reservoir sealed into the top of the syphon. These arrangements were necessary to prevent bubbles of gas blocking up the capillary.

The temperature was 20° ± 1·5°.

The Overvoltage of Zinc in N-*Sulphuric Acid.*

I. *Polished Zinc.*—In the first series of experiments a cathode was used the surface of which had been polished in a lathe with No. 0 sandpaper, an area of 10 sq. cm. being exposed. Initial experiments made by starting at the lowest current density, and

taking readings 2 minutes after each increase in current density, did not yield reproducible results. After an increase in current density, the overvoltage takes a considerable time to adjust itself to its maximum value. The readings in column I (Table I) were obtained by maintaining the current density on the cathode at its highest value (in this case 400 milliamps./cm.^{2}) and taking a reading after 10 minutes, and again 2 minutes after each successive lowering until the lowest current density was reached. This procedure was adopted throughout this work, as it was found to give the most consistent readings. The results in column II were obtained in the same way except that the current density was maintained at 40 milliamps./cm.^{2} for 30 minutes before the above procedure was followed. The figures show that prolonged electrolysis increases the overvoltage of polished zinc.

In the tables, current density (a) is given in milliamps./cm.^{2} and overvoltage (η) in volts.

TABLE I.

	Polished zinc.		Electrolytic zinc.			Polished zinc.		Electrolytic zinc.	
	I.	II.	III.	IV.		I.	II.	III.	IV.
a.	η.	η.	η.	η.	a.	η.	η.	η.	η.
400	1·23	1·32	1·28	1·275	40	1·11	1·175	1·15	1·13
300	1·21	1·29	1·26	1·25	30	1·10	1·155	1·14	1·12
200	1·185	1·26	1·23	1·215	20	1·085	1·135	1·12	1·10
100	1·16	1·23	1·19	1·18	10	1·05	1·09	1·08	1·07
75	1·14	1·21	1·17	1·16	5	1·00	1·04	1·02	1·005
50	1·12	1·19	1·16	—					

Each column shows the mean of several observations, the maximum deviation being $\pm$ 0·025 volt for columns I and II, and $\pm$ 0·01 for columns III and IV.

II. *Electrolytically-deposited Zinc.*—The surface of the cathode was mechanically polished as before. Electrolysis took place in 20 per cent. sulphuric acid, containing also 3 per cent. of zinc as zinc sulphate. The current density on the cathode was maintained at 0·10 amp./cm.^{2} for 10 minutes, the temperature being about 20°. The deposit was removed and a fresh one made between each series of readings, and the cathode washed free from zinc sulphate. In this way, a light grey, matt surface was obtained. The results are given in columns III and IV of Table I; the readings were taken in the same way as those in columns I and II, respectively.

The preliminary electrolysis seemed to have no effect in this case.

The Overvoltage of Zinc in Solutions containing Zinc Sulphate.

The surface of the cathode was formed by electrolytic deposition, as in the previous series of measurements. The electrolyte was

17 per cent. sulphuric acid containing different percentages of zinc as zinc sulphate.

TABLE II.

	η.					η.			
	17% H_2SO_4.	17% H_2SO_4. 0·01% Zn.	17% H_2SO_4. 0·10% Zn.	17% H_2SO_4. 1·0% Zn.		17% H_2SO_4.	17% H_2SO_4. 0·01% Zn.	17% H_2SO_4. 0·10% Zn.	17% H_2SO_4. 1·0% Zn.
a.					*a*.				
200	1·215	1·17	1·12	1·07	40	1·145	1·135	1·085	1·00
150	1·20	1·17	1·115	1·055	30	1·13	1·125	1·08	0·99
100	1·185	1·165	1·11	1·04	20	1·11	1·105	1·07	0·98
75	1·175	1·155	1·10	1·03	10	1·075	1·065	1·04	0·95
50	1·155	1·145	1·09	1·01	5	1·01	1·00	1·00	0·92

Even with the solution containing 0·01 per cent. of zinc signs of zinc deposition could be detected after a series of measurements. The amount deposited was very small in this case, however, and also from the 0·10 per cent. solution, but the metal separated from the 1·0 per cent. solution in considerable quantity.

With each solution, at all current densities, hydrogen appeared to be the main product. It can be seen from the figures (Table II) that the presence of zinc depresses the cathode potential considerably, the effect increasing with increase in zinc concentration.

The Effect of Metallic Impurities in the Electrolyte on the Overvoltage of Zinc.

Other observers have found that the cathode potential is depressed by the presence in the electrolyte, even in quite small concentration, of a metal having a lower overvoltage than that of the cathode material.

Table III gives some measurements of this effect. The cathode surface consisted of electrolytically deposited zinc. The zinc employed was unattacked by pure *N*-sulphuric acid. The copper and the iron (ferrous) were added in the form of sulphate, and the antimony as potassium antimonyl tartrate.

With the smaller concentration of copper, local action on open circuit was small but definite, and the surface of the cathode had finally a dull grey colour. The larger concentration of copper produced heavy local action on open circuit, the surface having a black, spongy appearance.

In the presence of iron moderate local action occurred on open circuit, the surface of the cathode becoming dull grey in colour.

The case of contamination with antimony is interesting. At high current densities, except with the larger concentrations employed, the depression of the overvoltage was very small. As the current

TABLE III.

a.	200.	100.	50.	20.	10.	5.
With 0·001% Cu : η ...	1·01	0·97	0·955	0·945	0·92	0·88
With 0·01% Cu : η	0·79	0·74	0·71	0·690	0·685	0·680
With 0·01% Fe : η	0·92	0·85	0·805	0·755	0·715	0·680

		η.			
a.	N-H_2SO_4.	+0·00033% Sb.	+0·0005% Sb.	+0·00075% Sb.	+0·001% Sb.
400	1·275	1·26	1·25	1·225	1·19
300	1·25	1·235	1·23	1·21	1·18
200	1·215	1·21	1·205	1·19	1·16
100	1·18	1·165	1·165	1·15	1·115
75	1·16	1·145	1·14	1·135	1·07
50	1·14	1·12	1·135	1·10	0·98
40	1·13	1·11	1·125	1·106	0·94
30	1·12	1·08	1·095	0·985	0·89
20	1·10	1·01	0·975	0·92	0·855
10	1·07	0·87	0·79	0·78	0·77
5	1·005	0·79	0·765	0·77	0·77

density decreased, however, a point was reached where the potential commenced to fall rapidly away from that found with the pure acid. This depression became larger, and commenced at a higher current density, as the concentration of antimony was increased. This suggests that at the higher current densities the antimony is removed as antimony hydride as soon as it is deposited, and an insufficient amount remains on the surface of the electrode to affect its electrochemical properties.

The Effect of the Addition of Gelatin to the Electrolyte.

A cathode having a surface of electrolytic zinc 20 sq. inches in area, was used in N-sulphuric acid at 20° containing varying quantities of gelatin.

TABLE IV.

Gelatin %	0.	0·01.	0·1.	0·5.	1·0.
			η.		
a.					
200	1·22	1·28	1·33	1·36	1·38
100	1·185	1·235	1·28	1·29	1·28
50	1·15	1·185	1·24	1·24	1·22
20	1·11	1·13	1·18	1·17	1·15
10	1·075	1·085	1·135	1·12	1·07
5	1·005	1·015	1·08	1·025	0·97

A small quantity of gelatin in the electrolyte increases the overvoltage of zinc. This increase is not proportional to the amount added. At high current densities, after a concentration of 0·1 per cent. has been reached, further addition of gelatin has little effect. At low current densities a maximum is reached, followed by a fall.

Effect of Temperature.

An electrode having a surface of electrolytically deposited zinc 10 sq. cm. in area was employed, the electrolyte being N-sulphuric acid.

TABLE V.

	η.					η.			
a.	20°.	40°.	60°.	80°.	a.	20°.	40°.	60°.	80°.
400	1·285	1·225	1·19	1·165	40	1·155	1·09	1·06	1·055
300	1·26	1·205	1·16	1·145	30	1·14	1·075	1·05	1·04
200	1·24	1·185	1·14	1·12	20	1·115	1·055	1·03	1·02
100	1·195	1·145	1·105	1·095	10	1·075	1·01	0·985	0·98
75	1·18	1·125	1·09	1·085	5	1·015	0·965	0·93	0·93
50	1·165	1·105	1·075	1·07					

The Overvoltage of Copper and Brass Cathodes.

These experiments were undertaken to ascertain whether there is any connexion between the overvoltage of a zinc cathode in an electrolyte contaminated with copper, and that of cathodes of pure copper or zinc–copper alloys.

The copper and brass cathodes were of the same dimensions as the zinc cathodes used in the experiments already described, and the same experimental procedure was followed.

The results were found to be difficult to reproduce, the effects of time, state of electrode surface, and previous history of the electrode being very marked.

Many series of measurements were made, and Table VI shows the maximum, minimum, and mean values of η obtained (1) with a drawn copper rod polished with No. 0 sandpaper and (2) with a cathode having a surface of electrolytically deposited copper, the electrolyte being N-sulphuric acid at 20°.

TABLE VI.

	Polished copper.			Electrolytic copper.		
a.	Max.	Mean.	Min.	Max.	Mean.	Min.
400	1·00	0·96	0·92	0·93	0·875	0·845
300	0·98	0·94	0·90	0·90	0·86	0·83
200	0·93	0·90	0·865	0·86	0·83	0·795
100	0·86	0·83	0·80	0·795	0·77	0·75
75	0·83	0·80	0·77	0·78	0·76	0·735
50	0·805	0·77	0·74	0·75	0·72	0·70
40	0·795	0·76	0·72	0·735	0·71	0·685
30	0·775	0·74	0·70	0·72	0·69	0·665
20	0·745	0·71	0·67	0·70	0·67	0·645
10	0·70	0·67	0·64	0·665	0·64	0·61
5	0·67	0·64	0·60	0·63	0·60	0·58

A brass cathode was cast from an alloy made by melting electrolytic zinc and electrolytic copper together in an earthenware crucible. The mould was a hollow tube of asbestos paper embedded

in silver sand. The cast metal cooled very slowly and contained 46·23 per cent. of copper and 53·42 per cent. of zinc. The surface was machined on a lathe and finished with No. 0 sandpaper.

TABLE VII.

Overvoltage of Brass in N-H_2SO_4 *at* 20°.

a.	Max.	Mean.	Min.	*a.*	Max.	Mean.	Min.
400	0·985	0·95	0·91	40	0·785	0·765	0·745
300	0·965	0·93	0·89	30	0·77	0·745	0·72
200	0·935	0·89	0·85	20	0·74	0·71	0·69
100	0·855	0·83	0·805	10	0·68	0·66	0 64
75	0·825	0·80	0·78	5	0·64	0·615	0·59

The overvoltage of brass appears to be the same as that of copper under the same experimental conditions. There seems to be no connexion between the overvoltage of zinc in solutions contaminated with copper and the overvoltage of copper or brass. The presence of a considerable amount of copper depresses the overvoltage of the zinc cathode below that of copper itself.

Theoretical.

The necessity of a certain overvoltage for the electrolytic liberation of hydrogen at a metal cathode surface can be explained by the existence of an unstable adsorption compound of the hydrogen deposited and the surface atoms of the cathode material, which spontaneously decomposes, yielding gaseous hydrogen. It is necessary to assume that the adsorbed hydrogen is capable of passing back into the ionic form (that is, it exerts a solution pressure), and also that the decomposition of the adsorption compound into gaseous hydrogen is irreversible; in other words, the adsorption layer cannot be reformed from gaseous hydrogen in contact with the electrode.

It can be seen that, in general, the higher is the overvoltage the higher will be the solution pressure of the adsorbed hydrogen, and therefore the greater will be the free energy, and consequently the instability, of the adsorption layer formed. It must be considered that each hydrogen-ion discharged, on losing its positive charge, becomes linked by valency forces to a surface atom of the electrode material. Two neighbouring hydrogen atoms thus bound then combine, and leave the surface as a molecule of hydrogen. The state of the hydrogen must be distinguished from that of chemical combination in the ordinary sense of the term, as it is only formed by virtue of the residual valency of the surface atoms.

These considerations readily explain the apparent connexion between overvoltage and catalysis. A metal with a high overvoltage would have no tendency to adsorb hydrogen, owing to the

unstable nature of the adsorption compound. When such a metal is placed in contact with hydrogen gas, the concentration of adsorbed hydrogen will be negligible, and there will be no possibility of catalytic action.

On the other hand, a metal having a low overvoltage would have a greater affinity for hydrogen, and the surface concentration of adsorbed hydrogen in equilibrium with gaseous hydrogen would be considerable. In this case, catalysis of a hydrogenation process could occur.

The efficiency of metals of high overvoltage in electrolytic reductions also follows. The ability of hydrogen to bring about these reductions depends on its free energy. If this is sufficiently high in the adsorbed layer for the reduction to be accompanied by a decrease in free energy, the reduction can take place.

The Variation of Overvoltage with Current Density.

The mathematical treatment of the above theory is here considered, and it should be noted that this does not give rise to an original set of equations; almost identical expressions were obtained by Tafel (*loc. cit.*) from somewhat different theoretical considerations. Consider 1 sq. cm. of electrode surface. Let C = the surface concentration of the adsorbed hydrogen, that is, the fraction of the total surface covered, if a unimolecular layer is postulated. Then the rate of decomposition of the adsorption layer is given by $-dC/dt = kC^2$, the rate of decomposition being proportional to the square of the surface concentration, since two adjacent hydrogen atoms are involved in the formation of a molecule of hydrogen. The rate of formation by the discharge of hydrogen-ions is given by $dC/dt = D_k k_1$, where D_k is the cathode current density and k_1 a constant. When equilibrium is attained, evidently $k_1 D_k = kC^2$, whence

$$C = \sqrt{k_1 D_k / k} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If P is the solution pressure of the adsorbed hydrogen, and P_H the osmotic pressure exerted by the hydrogen-ions on the cathode surface, the potential of a cathode from which hydrogen is being evolved will be given by $E = RT/F . \log (P/P_H)$. E_h, the equilibrium potential of the hydrogen electrode for identical hydrogen-ion concentration, and gaseous hydrogen at one atmosphere will be given by $E_h = RT/F . \log (P_{H_2}/P_H)$, P_{H_2} being the solution pressure exerted by gaseous hydrogen at one atmosphere. The overvoltage, η, is by definition $E - E_h$, whence

$$\eta = RT/F . \log (P/P_{H_2}) \quad . \quad . \quad . \quad . \quad (2)$$

Now P must be a function of the surface concentration of adsorbed

hydrogen. Assuming direct proportionality between P and C, one has $P = KC$, the value of K depending on the stability or free energy of the adsorption layer formed (and thus on the electrode material) and on the temperature. Substituting the value of C from equation (1), $P = K\sqrt{k_1 D_k/k}$; equation (2) then becomes

$$\eta = \frac{RT}{F} \log \left\{ K \sqrt{\frac{k_1 D_k}{k}} \cdot \frac{1}{P_{H_2}} \right\} \quad . \quad . \quad . \quad (3)$$

P_{H_2} is a constant, so that one has

$$\eta = \frac{RT}{F} \log \left\{ \frac{K}{P_{H_2}} \sqrt{\frac{k_1}{k}} \right\} + \frac{RT}{2F} \log D_k$$

or

$$\eta = \text{a constant} + RT/2F. \log D_k \quad . \quad . \quad . \quad (4)$$

As the surface of the electrode is assumed to be constant, one can write $\eta = a + b \log I$, where a and b are constants and I is the current passing. Tafel (*loc. cit.*) found this equation to hold with considerable accuracy for the mercury cathode; with other cathodes the agreement was not so close, although sufficiently good. In this research the equation was found to apply with fair accuracy to zinc, copper, and brass cathodes in pure sulphuric acid, but not under the other conditions investigated.

From equation (4) it can be seen that b should be equal to $RT/2F$, which has a value of 0·029 at 20°. In all the cases investigated by Tafel (*loc. cit.*) b had a value greater than $RT/2F$. This was confirmed in the present investigation. The values of b obtained were, for zinc 0·136, for copper 0·175, and for brass 0·171. Tafel suggested that this was due to k being a function of the current density. A more probable explanation is that a portion of the electrode surface is always covered with bubbles of gas. These separate electrolyte and electrode and diminish the effective surface available for electrolysis. When the current density increases, the fraction of the total surface covered with gas bubbles will increase also. As a consequence the effective current density will not be proportional to the current, but will increase at a greater rate, and thus the larger value of the constant b is explained. The fraction of the total surface covered would also be considerably affected by the most trivial variations in the state of the surface from experiment to experiment, and thus the difficulty of accurately reproducing overvoltage measurements would be explained.

The Diminution of Overvoltage with Time after the Breaking of the Circuit.

Owing to lack of time, no experimental work was done on this interesting subject. The matter was considered from a theoretical

point of view, owing to the possibility of its revealing the cause of the difference between the "direct" and the "commutator" method of measuring overvoltage.

The mathematical treatment given below follows directly from what has gone before.

For the decomposition of the adsorption layer after the cutting off of the electrolysing current we have $-dC/dt = kC^2$, whence $t = 1/kC + A$, where A is a constant.

Let C_0 be the value of C when $t = 0$, that is, the steady value existing before the current is broken. Then $A = -1/kC_0$ and $t = 1/k \,.\, (1/C - 1/C_0)$ or

$$\log C = \log C_0 + \log 1/(1 + ktC_0) \quad . \quad . \quad . \quad (5)$$

From the relation $P = KC$ and equations (2) and (5), we get

$$\eta = \frac{RT}{F} \log \frac{KC_0}{P_{H_2}} + \frac{RT}{F} \log \frac{1}{1 + ktC_0}$$

Writing η_0 for the first term (which is the value of η when t is zero) and substituting for C_0 the value obtained from equation (1), we find that

$$\eta = \eta_0 + \frac{RT}{F} \log \frac{1}{1 + kt\sqrt{k_1 D_k}/k}$$

Hence, by differentiation,

$$d\eta/dt = -\sqrt{kk_1 D_k}/(1 + t\sqrt{kk_1 D_k}).$$

When $t = 0, d\eta/dt = -\sqrt{kk_1 D_k}.$

When $t = \infty, d\eta/dt = 0.$

If these relations hold, the values obtained by the commutator method of measuring overvoltage should be lower than those obtained by the direct method and should be dependent on the commutator speed. This behaviour has been observed by recent workers on overvoltage, notably by Dunnill (J., 1921, **119**, 108) and by Glasstone (J., 1923, **123**, 1745, 2926; this vol., p. 250).

Summary.

The overvoltage necessary to liberate hydrogen electrolytically at a zinc cathode under various conditions has been studied.

For a zinc cathode in pure sulphuric acid the equation $\eta = a + b \log D_k$ has been found to apply, η being the overvoltage, D_k the current density, and a and b constants. The effect of the presence of certain metallic impurities on the cathode potential of the zinc electrode has been investigated. The overvoltage of zinc at different temperatures and in the presence of gelatin, added to the electrolyte, has been measured.

The theoretical aspect of overvoltage has been discussed, and an expression has been obtained showing the way in which overvoltage falls off with time after the breaking of the circuit.

I desire to express my indebtedness to Professor F. G. Donnan for suggesting and directing this research, which was carried out in the Sir William Ramsay Laboratory of Physical Chemistry at University College, London, and to the Department of Scientific and Industrial Research for a grant enabling this work to be undertaken.

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RESEARCH DEPARTMENT,
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CXXXIII.—*Optical Activity and the Polarity of Groups Attached to the Asymmetric Atom. Part I.*

By HAROLD GORDON RULE.

IN the early nineties of the last century Crum Brown and Guye independently advanced the suggestion that the magnitude of rotation of an optically active compound was related quantitatively to the asymmetry of the molecule. Whilst Guye calculated the degree of asymmetry from the relative masses of the four radicals united to the asymmetric atom and the distances of their respective centres of gravity from the centre of the tetrahedron, Crum Brown (*Proc. Roy. Soc. Edin.*, 1890, 181), on the other hand, attached to each radical a value κ, which is stated to be a function of the composition and constitution of the radical. The hypothesis of Guye, although holding approximately for the variation of alkyl groups in certain ester series, failed entirely under a more searching examination, and so far no means of attaching a definite physical significance to Crum Brown's value κ has been suggested. During the last thirty years the advance in our knowledge of the factors governing optical rotation has been slow. It has long been known that the presence of unsaturated linkings tends to increase the rotation and that the specific effect of a given group changes gradually as it becomes further removed from the asymmetric atom. In the case of certain active carbinols, Pickard and Kenyon (J., 1913, **103**, 1923) have shown that an exaltation of activity is produced as the alkyl chain increases to five or a multiple of five carbon atoms in length. In addition, interesting numerical relation-

ships have been shown to exist in the sugar series by Hudson and by Anderson (*J. Amer. Chem. Soc.*, 1910—1919).

For some years past chemists have been slowly feeling their way towards a true appreciation of the relative polarity of atoms and groups, as exhibited in the chemical and physical properties of compounds. A strong lead in this direction has been given by the work of Vorländer, Flürscheim, and Michael, among others, with results which prepared the way for the theory of induced alternate polarity put forward by Lapworth (*Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 1) and subsequently deduced theoretically by Lapworth (J., 1922, **121**, 461), Kermack and Robinson (*ibid.*, p. 427), and J. J. Thomson (*Phil. Mag.*, 1923, [vi], **46**, 497) independently.

Up to the present little has been known respecting the relative polarity of groups, but some information on this point may be gained from an examination of benzene substitution data. Holleman (" Die direkte Einführung von Substituenten in den Benzolkern," 1910, p. 199) quotes figures showing the proportions of *o*-, *m*-, and *p*-isomerides formed by the nitration of certain simple mono-substituted benzenes under comparable conditions. On arranging the substituent groups so as to represent a gradual transition from those strongly para- to those strongly meta-directive, we obtain the series (OH), F, Cl, I, Br, CH_3, H, CO_2H, NO_2. Probably the hydroxyl group should head the list with fluorine, since phenol yields no *m*-nitrophenol, but here, as in a number of other cases, substitution may be mainly indirect. The unexpected inversion of Br and I is possibly due to experimental inaccuracy, but otherwise it may be concluded that the above series indicates the relative polarities of the groups as we pass from the highly negative hydroxyl to the strongly positive nitro-group.

A more fundamental method of determining the relative polarity of groups of simple structure is to compare the specific inductive capacities of compounds of the type RX for long wave-lengths. Thomson (*loc. cit.*) considers the replacement of a hydrogen atom in a hydrocarbon chain by a positive and a negative group respectively in its effect on chemical reaction. He shows that substitution by a negative group such as CH_3 or OH is equivalent to the introduction of an electric doublet with its positive end at the carbon atom of the parent molecule and its negative end at the substituent group. Conversely, substitution by a positive group such as NO_2 or CO_2H is equivalent to introducing an electric doublet with its negative end at the carbon atom of the parent molecule and its positive end at the substituent group. In consequence, an electrostatic moment is introduced into the molecule which in turn affects

the specific inductive capacity of the compound, and the change in the capacity is the measure of the moment.

If now we compare the specific inductive capacities * of compounds of the type C_2H_5X for long wave-lengths and at normal temperatures, and correct the values for molecular weight and density (compare Thomson, *loc. cit.*), we find that the influence of the groups is in the order $NO_2 > CN > CO{\cdot}CH_3 > OH > CHO > Cl > Br > I >$ alkyl. Similarly, from the figures available for the series C_6H_5X, we find $NO_2 > CN > CO{\cdot}CH_3 > CHO > Cl > Br > Et > Me > H$. On rearranging these groups to represent a gradual transition from high negative to high positive polarity, we obtain the sequence

$$\overset{-}{OH},\ Cl,\ Br,\ I,\ Et,\ \overset{-}{Me},\ \overset{+}{H},\ CO_2H,\ CHO,\ CO{\cdot}CH_3,\ CN,\ \overset{+}{NO_2},$$

in which the place of the carboxyl group is determined by the figures recorded for acetic and propionic acids. The methoxy- and amino-groups appear to fall in the neighbourhood of bromine and iodine, but here and in other cases the positions are variable and the values require revision.

It will be observed that, except for the inversion of Br and I, the series deduced from benzene substitution data agrees with the above. Further confirmation may be obtained from the influence of various groups on the dissociation constants of substituted acetic (or benzoic) acids, from which in the same manner may be derived the sequence

$$Cl,\ Br,\ I,\ OMe,\ OH,\ Me,\ H,\ CO_2H,\ CN,\ NO_2.$$

Here the hydroxyl group has undergone a considerable displacement, although the remaining groups occupy the same positions as in the series obtained from inductive capacities.

Subject to minor variations, therefore, the relative polarity of the groups is independent of the particular physical property from which it has been deduced, and accordingly we have here a natural sequence based on electrochemical character and analogous to the well-known electromotive force series for the metals. In the following pages the series deduced from inductive capacities will be referred to as the polar series.

In view of the above regularities, it is probable that a similar relationship exists between the polarity of a substituent group and its influence on optical rotation. Thomson (*loc. cit.*) states that the intense electric field due to the introduction of a radical such as Cl or OH will bring about a change in the distribution of electrical forces in and around the molecule. On the provisional assumption that one of the factors governing optical rotation is the electric

* The following series are based on the physical constants given in Landolt Börnstein's Physikalisch-chemische Tabellen (1923).

field exerted at the asymmetric atom by the attached side chains, it would be anticipated that the influence of a substituent group on the molecular rotation of a compound would depend in sign and magnitude on the polarity of the group. Further, since an alternate induced effect does not appear to be transmitted appreciably through a saturated chain of carbon atoms, the influence of a group will be the greater the nearer it is to the asymmetric atom. On attempting to trace this relationship, however, we are immediately confronted with the abnormalities introduced by the use of a solvent in the measurement of specific rotation.

Molecular Rotations in the Presence and Absence of a Solvent.

In spite of the now well-recognised influence of solvent on optical rotation, it is a curious fact that the great majority of comparative measurements of group effect have been estimated in the presence of one solvent alone, and in those cases in which two or more solvents have been employed it is to be observed that the sequence sometimes varies with the solvent. Deductions drawn from determinations of this nature are therefore open to criticism. A most interesting example of solvent action is furnished by the cases of *d*-β-octyl acetate and *d*-octan-β-ol (Pickard and Kenyon, J., 1914, **105**, 835). The molecular rotation of the acetate in absence of solvent is $[M]_D = +11{\cdot}77°$. Of the fourteen solvents used by these authors, ethylene dibromide raised this figure to $+16{\cdot}84°$, and the other thirteen exerted the reverse effect, and produced continuously varying values through zero to $[M]_D = -15{\cdot}42°$ (carbon disulphide). With the pure carbinol $[M]_D = +12{\cdot}85°$, on the other hand, these solvents tend to bring about a change in the opposite direction, in general raising the positive rotation, which is highest in carbon disulphide. Obviously there is here no possibility of comparing the influence of the –OH, $-O{\cdot}CO{\cdot}CH_3$ and other groups on the activity of the β-octyl complex in the presence of a solvent. The only method at present available is to compare the rotations of these substances in the liquid state. In this connexion, Pickard and Kenyon have shown that the molecular rotations of the pure carbinols remain unaltered when measured in the presence of the corresponding inactive carbinols. The molecular rotations of certain menthyl esters of substituted benzoic acids have also been examined in a number of solvents (Pickard and Kenyon, J., 1915, **107**, 52), with results showing that in the majority of these cases the presence of a solvent produces little alteration in rotation. Nevertheless, the relative order of the rotations is frequently changed. In benzene, for example, we find the sequence *p*-iodo-ester (– 269°), *p*-fluoro-ester (– 241°), and the unsubstituted

compound (— 234°), whereas in the liquid state the order is unsubstituted ester (— 239°), *p*-fluoro-ester (— 237°), and *p*-iodo-ester (— 237°). Again, the activity of some derivatives of phenyliminocamphor has been determined by Singh and Mazumder (J., 1919, **115**, 567) in testing the validity of Frankland's "lever-arm" theory, some of the rotations in this case being quoted for two solvents. With meta-substitution, for example, the influence of the groups is in the order, in chloroform solution, $Cl = Br < CH_3 < H$, and in methyl alcohol solution, $Cl = Br < H < CH_3$. The displacement of the hydrogen compound is repeated in the para-series where, in chloroform solution, $Br < H < CH_3$, and in methyl alcohol solution, $H < Br < CH_3$. In each case, the displacement of the hydrogen compound is comparatively large. The above examples therefore emphasise the desirability of instituting such comparisons wherever possible with compounds in the liquid state. Conclusions drawn from determinations in solution are more likely to be correct if a variety of solvents is employed.

Among liquid or readily fusible optically active compounds recorded in the literature are derivatives of lævorotatory *d*-amyl alcohol and various esters prepared from active acids and alcohols. The molecular rotations of a number of these are collected in Tables I to IV below. Other figures relating to determinations in the presence of solvents are to be found in Table V. Except where otherwise stated, the figures are arranged in their relative order of magnitude and all quotations refer to normal temperatures.

TABLE I.

Molecular rotations of derivatives of lævorotatory *d*-amyl alcohol in the absence of solvent ($R = C_4H_9$).

Compound.	$[\alpha]_D$.	$[M]_D$.	Reference.
$R \cdot CH_2 \cdot OH$	−5·90°	−5·19°	Marckwald and McKenzie, *Ber.*, 1901, **34**, 490.
$R \cdot CH_2 \cdot NH_2$	−5·86	−5·10	Marckwald, *Ber.*, 1904, **37**, 1045.
$R \cdot CH_2 \cdot O \cdot CH_3$	+0·40	+0·41	Welt.
$R \cdot CH_2Cl$	+1·70	+1·81	McKenzie and Clough, J., **1913**, **103**, 699.
$R \cdot CH_2Br$	+3·68	+5·56	Marckwald, *loc. cit.*
$R \cdot CH_2 \cdot C_2H_5$	+6·23	+6·23	Welt, *Compt. rend.*, 1894, **119**, 743.
$R \cdot CH_2I$	+5·64	+11·17	Marckwald, *loc. cit.*
$R \cdot CO_2H$	+17·85	+18·21	Marckwald and McKenzie, *loc. cit.*
$R \cdot CH_2 \cdot CO_2H$	+8·92	+10·35	Romburgh, *Rec. trav. chim.*, **1886**, **5**, 222.
$R \cdot CH_2 \cdot CH_2 \cdot CO_2H$	+8·44 (+10·41)	+10·97 (+13·53)	Walden, *Z. physikal. Chem.*, **1894**, **15**, 642 (from amyl alcohol of $[\alpha]_D = -4·78°$).

The specific rotations quoted for hexoic acid (8·92°) and heptoic acid (8·44°) are probably too low. The latter compound together with amyl iodide and a number of other derivatives was prepared by Walden from amyl alcohol of $[\alpha]_D = -4·78°$ and thus of 81 per

cent. purity. The value obtained for the iodide was + 4·55°, which when corrected for an alcohol of $[\alpha]_D = -5·9°$ gives + 5·62°, in close agreement with the value + 5·64° determined later by Marckwald (*loc. cit.*), who was using the pure alcohol. Similarly, corrected figures for heptoic acid are given in brackets in the above table. Hence it is to be concluded that the specific rotation found for hexoic acid by Romburgh is low and that the true value should lie between 10·41° and 17·85°, bringing its molecular rotation well above that of amyl iodide. It will thus be seen that CO_2H, the only positive group contained in the list, stands at one extreme with the highly negative hydroxyl group at the other, and with the exception of a reversal in the position of C_2H_5 and I the negative groups are arranged in the order of their relative polarities so far as can be judged from the above polar series. A comparison of the rotations of the carboxylic acids shows that as the positive $-CO_2H$ group is brought nearer the asymmetric carbon atom its influence becomes more marked, displacing the rotation still further away from the value due to the presence of the strongly negative hydroxyl group.

TABLE II.

Molecular rotations of the menthyl esters of mono-substituted benzoic acids, $C_6H_4X·CO_2H$, in absence of solvent.

X.	*o*-.	*m*-.	*p*-.	X.	*o*-.	*m*-.	*p*-.
$O·CH_3$	−148°	−247°	−250°	I	−237°	−237°	−237°
F	−194·5	−236	−239	H	−239	−239	−239
Cl	−195	−237	−237	*CO_2H	−332	—	−259
Br	−205	−239	−239	NO_2 (at 65°)	−381	−251	−235
CH_3	−231	−240	−246				

* J., 1918, **113**, 57.

The mono- and di-substituted esters of this type examined by Cohen (J., 1914, **105**, 1892) form one of the most remarkable illustrations of the influence of substituent groups on optical rotation. It will be observed that the only marked differences are those occurring in the ortho-series, where the replacement of hydrogen by a negative group lowers the rotation and substitution by a positive group raises the value. Except for a reversal in the positions of CH_3 and I (compare also Table I), the order of the groups is in close agreement with the polar series deduced above. The rotations of the meta- and para-derivatives do not differ greatly from that of the unsubstituted compound.

Among the *o*-disubstituted benzoic esters prepared by Cohen the following may be mentioned:

2 : 6-Dinitro-derivative	(in benzene at 20°)	$[M]_D$ −642°
2 : 6-Chloronitro-derivative	(at 100°)	,, −237
2 : 6-Dichloro-derivative	(at 100°)	,, −32·5
Menthyl benzoate	(at 100°)	,, −233

These figures indicate clearly that groups of like polarity reinforce each other in the ortho-position, whilst the introduction of a positive and a negative group, both of marked polarity, leaves the rotation of the unsubstituted ester comparatively unaltered. With respect to the nitro-derivative, Cohen has remarked that the high rotation due to the presence of this group is still further exalted in benzene solution.

TABLE III.

Molecular rotations of the complex $CH_2X{\cdot}COO$-menthyl in absence of solvent.

X.		Reference.
H	153·7°	Tschugaev.
CH_3	160·2	,,
C_2H_5	159·5	,,
Br	169	(,,) Hilditch, J., 1912, **101**, 202.
Cl	171	Hilditch, *loc. cit.*

Once again the influence of the substituent groups is in agreement with their polarity. It is also interesting to note the result of replacing the methyl group in menthyl acetate with the positive hydrogen atom and the comparatively strongly negative amino-group respectively. The rotations for menthyl formate, acetate, and carbamate are given below, the value for the carbamate in chloroform solution being quoted:

Menthyl formate	$[M]_D$	−146°
Menthyl acetate	,,	−153·7
Menthyl carbamate	,,	−170 (Arth, *Ann. Chim. Phys.*, 1886, [vi], **7**, 464).

The position of the amino-group is not indicated in the above polar series, but it is undoubtedly more strongly negative than the methyl group, as shown, for example, by the "molecular" inductive capacities, the value for aniline being 6·7, for toluene 2·4, and for benzene 2·0.

TABLE IV.

Molecular rotation of the complex $CH_3{\cdot}CHX{\cdot}CO_2Et$ in the absence of solvent.

X.	$[\alpha]_D$.	$[M]_D$.	
OH	14·5°	17·11°	J. W. Walker, J., 1895, **67**, 916.
NH_2	Extremely low.		E. Fischer, *Ber.*, 1907, **40**, 500.
Cl	19·5	26·52	J. W. Walker, *loc. cit.*
Br	31·5	57·02	,, ,, ,,

Without entering into the debatable point as to whether NH_2 precedes or follows OH in this series, it is seen that the groups fall into the order (OH, NH_2), Cl, Br, in general agreement with their polarity.

TABLE V.

Molecular rotations of bromo- and nitro-derivatives of *d*-camphor in solution.

	$[\alpha]_D$.	$[M]_D$.
α-Bromocamphor	+139° (in alcohol)	+321·0°
β-Bromo „	+29·4 (in alcohol)	+67·9
d-Camphor	+55 (in alcohol)	+83·6
α′-Nitrocamphor	−6·0° (in alc.) (Cazeneuve).	−104° (in benzene) Lowry, J., 1898, **73**, 986.	−11·8° (alc.) (benzene) −205°.

The chemistry of the camphor derivatives is still in a very confused state, and many of them, such as nitrocamphor, exhibit mutarotation. Nevertheless, the above figures relating to some of the best investigated of these compounds serve to illustrate the fact that the negative bromo- and the positive nitro-groups tend to influence the rotation of the parent substance in opposite directions.

In the expectation of finding some points of resemblance between optical activity and magnetic rotation, the values for the latter determined by Perkin (J., 1896, **69**, 1236) for benzene and a number of its monosubstituted derivatives have been collected together in the following table, in which the values in the left-hand column are greater than that of benzene itself.

TABLE VI.

Electromagnetic rotations of monosubstituted benzene derivatives compared with water.

Value for benzene = 11·284°.

Substituent.		Substituent.	
$N(CH_3)_2$	20·567°	CO_2H	10·424°
I	19·108	F	9·970
NH_2	16·076	NO_2	9·361
Br	14·506		
$O{\cdot}CH_3$	13·958		
Cl	12·51		
CH_3	12·157		
OH	12·140		
CHO	11·864		
CN	11·853		
		$C_6H_5{\cdot}CO{\cdot}CH_3$	12·597°
		$C_6H_5{\cdot}CO{\cdot}C_6H_5$	23·375

In spite of the strongly additive nature of the property under consideration, there is a distinct tendency for the groups to arrange themselves according to their polar character, particularly where those of low atomic or molecular weight are concerned. It will be observed that the positive NO_2, CO_2H, H, CN, and CHO groups fall

together at the bottom of the list, the negative groups assuming higher positions. As already observed by Perkin, the rotation of fluorobenzene lies abnormally low, a peculiarity which may possibly be connected with the unexpected position of the fluorine compound in approximating so closely to that of chlorine in Table II.

Bearing of the Electrostatic Moment on the Rotation of Substituted Benzene Derivatives.

The evidence collected in the foregoing tables suggests that the conception of a mechanical moment tentatively advanced in the "lever-arm theory" by Frankland should be replaced by that of an electrostatic moment. In order to test this new hypothesis, we require to know the influence of a second substituent group on the electrostatic moment of a monosubstituted benzene. No measurements relating to the specific inductive capacities of compounds of this type have as yet been recorded, but Thomson (*loc. cit.*) has discussed the problem from a theoretical point of view in connexion with chemical reactivity. He concludes that with two similar substituents in the benzene nucleus the specific inductive capacity of the para-compound is low, the electrostatic moment of the one group being in opposition to that of the other. Meta-substitution leaves the moment of the monosubstituted molecule unchanged, and ortho-substitution raises the value. On the other hand, if the second substituent is of different type from the first, the values will be in the reverse order. From this it follows that with two substituents of similar polarity the electrostatic moments should be in the order $o>(m,\ \mathrm{H})>p$, where H represents the original monosubstituted compound, and with two substituents of opposite polarity in the order $p>(m,\ \mathrm{H})>o$.

On the view advanced in the earlier part of this paper that the influence of a substituent on the optical rotation of a parent compound is dependent in sign and magnitude on the change in electrostatic moment, these considerations lead at once to the following conclusions: (1) The molecular rotations of a substituted benzene derivative will either be of the order $p>m>o$ or $o>m>p$, and not in the former sequence alone as required by the suggestion of Frankland. (2) The sequence found with a negative substituent will be the reverse of that found with a positive substituent. (3) The value for the unsubstituted compound will in each case be between those of the *o*- and *p*-derivatives. So far as can be judged, this is in close agreement with the experimental facts and with the absence of any definite evidence relating to an alternate effect in the activity of *o*-, *m*-, and *p*-substituted benzene derivatives.

Before attempting to predict the direction in which a given substituent will affect the rotation of a benzene derivative, it should be noted that the change in the electric field at the asymmetric atom following on the introduction of a substituent of complex structure may bear little relationship to the change in the electrostatic moment of the molecule as a whole, the former being largely dependent on the disposition and character of the atoms in the immediate vicinity of the asymmetric atom. Moreover, the work of Hilditch (J., 1909, **95**, 1581) on the menthyl esters of dicarboxylic acids and of Pickard and Kenyon (*loc. cit.*) on the active carbinols has indicated that the optical rotation of compounds containing long chains of atoms is influenced by the actual configuration of these chains in space. By confining our attention to the change in rotation produced by substitution in one part of the molecule, however, it is often possible to foresee the result of further substitution at this point. In the majority of cases under examination this involves comparison with the hydroxy-derivative as standard, and introduces an additional complication. It might have been anticipated that the substitution of a hydroxylic hydrogen atom by a negative alkyl and a positive benzoyl group respectively would influence the rotation in opposite directions. The hydroxyl group, however, is represented by Thomson as wholly enclosed in a sheath of electrons and in consequence the replacement of the hydrogen atom by a complex such as the alkyl or benzoyl group must bring about a change of fundamental character, irrespective of the fact that these groups fall on opposite sides of hydrogen in the polar series. In actual practice, the moments of the alcohols, as determined from inductive capacity, are much greater than those of their ethers or esters, and similarly the molecular rotations of amyl alcohol or menthol lie well outside the values recorded for their respective ethers and esters.

Considering now the case of the menthyl benzoates in Table II, the presence of the positive benzoyl group has introduced an electrostatic moment of opposite orientation to that of the negative hydroxyl group of the parent menthol, and this change is accompanied by a large increase of negative rotation.* Any substituent which still further increases the characteristic moment of the benzoyl group should therefore still further increase the rotation. Conversely, any group tending to decrease this moment should decrease the rotation of the ester. As the benzene nucleus already contains one positive substituent, the introduction of a positive group should increase the moment in the *o*-position and decrease it

* Part of this increase is probably due to the unsaturated character of the benzene nucleus.

in the *p*-position. The predicted rotations for a positive group are therefore $o>(m, H)>p$, and for a negative substituent $p>(m, H)>o$.

Reference to the figures quoted in Table II shows that this is in agreement with the influence of the groups NO_2, CH_3, and $O{\cdot}CH_3$. With the omission of the carboxy-derivative, which forms a partial exception, it is found that the remaining *m*- and *p*- values do not vary more than two or three units from that of the unsubstituted compound—a difference which is probably of the same order as the experimental error. The methoxy-, ethoxy-, propoxy-, and *iso*amyloxy-compounds (Cohen, *loc. cit.*) were compared in the liquid state at 100°, and the observed rotations are again in close agreement with the above conclusions :

	$O{\cdot}CH_3$.	$O{\cdot}C_2H_5$.	$O{\cdot}C_3H_7$.	$O{\cdot}C_5H_{11}$.
o-	−155°	−157°	−180°	−196°
m-	−243	−237	−235	−237
p-	−239	−238	−234	−237

For menthyl benzoate, $[M]_D^{100°} = -233°$.

The argument in the case of the amyl benzoates and the methyl dibenzoyltartrates (Frankland, Carter, and Adams, J., 1912, **101**, 2470) is similar. In the former instance, the introduction of the benzoyl complex alters the rotation of amyl alcohol from **− 3·87°** (representing an impure product) to + 9·52°, and is thus equivalent to an increase in positive rotation. The presence of a negative group in the *p*-position enhances still further the moment due to the benzoyl group and should produce an increase of positive rotation, leading to the prediction $p>(m, H)>o$. As quoted by Frankland, the values for the molecular rotations of the toluic and bromobenzoic esters of amyl alcohol are :

	o.	*m*.	*p*.
Benzoate		+9·52°	
Toluates	+9·37°	+10·41	+10·71°
Bromobenzoates	+5·09	+7·32	+8·62

Methyl groups and bromine atoms thus give rise to the expected sequence $p>m>o$. The hydrogen compound occupies an intermediate position in the toluates, but in the bromobenzoates lies just above the *p*-value, a deviation which may be due to the impurity of the initial material.

In the methyl dibenzoyltartrates the case is identical with that just quoted, leading again to the predicted sequence $p>(m, H)>o$. Reference to the following figures shows this to be in excellent agreement with fact.

Influence of substituent groups in the benzene nuclei on the rotation of methyl dibenzoyltartrate ($[M]_D^{100°}$) :

	o.	*m.*	*p.*
H		−280°	
CH_3	−282°	−327	−426°
Cl	−212	−352	−445
Br	−176	−376	−500
I	−105	−431	[−606]

It will be observed that the four negative groups all produce a similar effect on the rotation, but that the halogens are in the reverse order of their relative polarities as deduced in the polar series.*

An illustration of a different type is that furnished by the phenyl and tolyl amyl ethers. The substitution of the phenoxy-group for the hydroxyl group of amyl alcohol represents the introduction of an electrostatic moment of lower magnitude but the same sign, and converts the negative rotation of the alcohol into a positive rotation. A substituent which still further diminishes the (negative) moment due to the phenoxy-group should therefore still further increase the positive rotation. Since the original substituent in the nucleus is negative, this condition should be fulfilled by a methyl group in the *p*-position and the magnitude of the rotations of the tolyl ethers would be expected to be in the order $p > (m, H) > o$. The specific rotations quoted by Landolt ("Das optische Drehungs vermögen," 2nd edn.) are

o.	*m.*	*p.*
+3·86°	+3·93°	+4·26°

Phenyl amyl ether is quoted at 4·01°, which brings its molecular rotation (6·6°) just below that of the *o*-tolyl derivative (6·9°). The compounds, however, were prepared at a comparatively early date in the history of optical activity and from an impure alcohol.

A more complicated example is that of the substituted dianilides of tartaric acid examined by Frankland and Twiss (J., 1910, **97**, 155). The data at our disposal are not sufficient for a prediction based on the alteration in moment of the original carboxyl groups of tartaric acid, but we may confine our attention to the change produced by the substitution of $-NH\cdot C_6H_5$ for the carboxylic –OH. This change (see below) brings about a great increase in positive rotation and represents a diminution of the original (negative) moment due to the hydroxyl group.† A substituent which still further diminishes this moment should still further increase the positive rotation. We should thus expect, with a negative sub-

* The rotations of the ethyl dinitrobenzoyltartrates vary strongly with temperature (Frankland and Harger, J., 1904, **85**, 1571), the sequence changing several times between 20° and 185°.

† The inductive capacity of the compound R·OH is very much greater than that of $R\cdot NH\cdot C_6H_5$.

stituent, $p>(m, H)>o$, in agreement with the figures found by the above authors, who investigated the methyl and halogen derivatives. $[M]_D^{20°}$ was measured in pyridine solution.

	o.	*m.*	*p.*
H	—	+739°	—
CH_3	+667°	+730	+793°
Cl	+709	+824	+838
Br	+652	+867	+886

For a more searching test of the electrostatic moment theory, it is obviously desirable that the influence of more substituents of positive polarity should be determined, conclusive evidence for both positive and negative groups being available only in the very complete investigation of the menthyl benzoates carried out by Cohen.

Summary and Conclusion.

The relative polarity of certain simple groups as deduced in the earlier part of this paper from data referring to benzene substitution, dissociation constants, or specific inductive capacity is applied to the influence of these and other groups on optical activity.

In general, it is found that the replacement of a hydrogen atom in an optically active compound by a positive substituent displaces the rotation in the opposite sense to that due to a negative substituent, and that the magnitude of the displacement corresponds more or less closely to the position of the substituent in the polar series, so far as this can be judged from the limited data at our disposal. This correspondence is most readily observed in the case of liquid compounds where the rotation can be measured in the absence of a solvent.

A similar distinction between substituents of positive and negative polarity may be traced in their influence on the electromagnetic rotation of benzene.

With optically active compounds containing a complex group of the type C_6H_5X, it is shown that a second substituent in the benzene nucleus should influence the rotation in the order $p>(m, H)>o$ or $o>(m, H)>p$, where H represents the original group, and that the sequence for a positive substituent should be the reverse of that for a negative one. Further, if the specific influence of the group C_6H_5X on the rotation is known, the actual direction of the displacement due to the second substituent can be predicted in a number of cases.

The possibility is not excluded that the major influence due to a given group is accompanied by a minor one of alternate nature and that the latter might become more evident under favourable con-

ditions. Indications of a similar dual effect are to be observed in connexion with the ionisation of phenols and carboxylic acids.

Optical activity presents a problem of great complexity and involves a number of other factors, including temperature and the wave-length of the light employed. Hence it is scarcely to be expected that an unfailing regularity will be found by following a single variable. The above evidence, however, suggests that the κ of Crum Brown is some function of the electrostatic moments due to the constituent parts of the chain attached to the asymmetric atom.

In order further to test the above views, it is proposed to make a more detailed examination of the influence of positive and negative substituents on optical activity, especially of compounds in the liquid state.

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CXXXIV.—*Colour and Molecular Geometry.*

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FOR the dicyclic family of coloured substances there is a relationship between change of colour and change of distance as measured in the molecule between two points which are positive (Moir, T., 1921, **119**, 1657; 1922, **121**, 1811). Owing to our former ignorance of the real size and shape of the benzene molecule, it was impossible to put the monocyclic colour family on a similar physical basis, using plane formulæ, and it was seen that the distance between the para-positions in benzene must be considerably smaller than is the case in a plane hexagon. Sir W. Bragg's elucidation of the real size and shape of the benzene molecule has now enabled me to clear up the discrepancy and to find a method of calculating the colour of standard substances of all classes by the application of trigonometry and algebra to the (three-dimensional) picture of the molecule.

Bragg's benzene picture is a skew-hexagon (T., 1922, **122**, 2783) of which all the sides are equal and all the angles are 109° 28′. It lies in three different planes, and the para-position distance is about the same as the ortho-position distance.

Bragg's figure will not serve as a true picture of the benzene

molecule: it must be modified by getting rid of six valencies. In other words, Bragg's figure must be made to correspond to Lapworth's centric electronic diagram, and to do so the original cubic octet of carbon must be rearranged as in Fig. 1. Two trios of electrons lie at opposite ends of a face-diagonal of the cube, and the remaining pair outside the centre of the opposite face of the cube.

The plane ABDC has then the appearance of Fig. 2.

The angle AOC can be shown to be 109° 28′ as required by Bragg, and the arrangement of the electrons is also correct. O, being the centre of the cube, represents also the centre of the carbon atom, and OA represents the radius of the carbon atom, equal to 0·77 tenth-metre according to Bragg. Since $AB = AD/\sqrt{3}$, $OE = R/\sqrt{3}$, where R is the carbon-atom radius. This direction OE represents the direction of the attachment of the hydrogen atom in benzene from the centre of the carbon atom. It is probable, however, that the attachment of the hydrogen atom is not so near as E to the centre of the carbon atom. Suppose it at E′, intermediate between the cubic and the spherical surface of the carbon atom.

For stability, the attraction of the positive nucleus at O for the six electrons at A and C should be balanced by the attraction for the pair at E′.

Hence $$\frac{6e\cos(AOC/2)}{R^2} = \frac{2e}{OE_1^2}, \text{ whence } OE_1 = R \div \sqrt[4]{3}.$$

Since R is 0·77 tenth-metre, $OE_1 = 0{\cdot}58$ tenth-metre. This, then, is the probable distance from the carbon centre at which the "surface" of the hydrogen atom is attached.

Bragg's benzene formula thus becomes as in Fig. 3, in which A and C represent the junction of carbon to carbon and E_1 the junction of hydrogen to carbon. Only the para-hydrogen junctions are shown in the diagram.

The breadth of the figure through H is $1{\cdot}54 \times 2 \sin AOC/2 = 2{\cdot}51$ Å., in agreement with Bragg's measurement of the width of the benzene skeleton as exemplified in the difference between anthracene and naphthalene [although OO′ (see below) suits equally well].

The cross section of the benzene molecule in the plane containing the para-hydrogen valencies has the form of an equally sloped trapezium (see Fig. 4).

The angles OHH_1 and O_1H_1H are 125° 16′ ($\cos^{-1} - 1/\sqrt{3}$); $HH_1 = 1{\cdot}54$ Å.; $OH = O_1H_1 = 0{\cdot}89$ Å.; $E_1H = E_{11}H_1 = 1{\cdot}47$ Å.; $OO' = 2{\cdot}56$ Å.; and $E_1E_{11} = 3{\cdot}23$ Å. These are the dimensions of the C_6H_4 group with para-positions unoccupied.

Benzene itself is shown in Fig. 5 with the addition of two lines

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

showing the intersection of the directions of the para-valencies below the molecule. These directions meet at an angle θ, which is 180° minus the tetrahedral angle 109° 28′. The distance between the centres of the para-hydrogen atoms is 3·82 Å.

Application to the Calculation of Colour from Distances in the Molecule.

In monocyclic coloured substances one of the hydrogen atoms of benzene is replaced by an auxochrome and the other by a hapton. In very simple compounds auxochrome and hapton may be the same, for example, in ionised quinol or *p*-phenylenediamine, such "unloaded" compounds being coloured only as regards ultra-violet light.

The position of the absorption band is governed by the distance between the centres of auxochrome and hapton measured in a straight line through the molecule, and also (in subordinate measure) by the eccentricity of the ellipse of motion of the electron which is revolving round the two positive centres of force resident in the atomic nucleus of hapton and auxochrome (or rather their characteristic elements C, N, O, and S).

Roseveare's equation (T., 1922, **121**, 1810) rewritten becomes :

$$T = \pi\sqrt{\frac{2a^3}{\mu}}\left[1 - \frac{3}{1}\left(\frac{1}{2}\right)^2 e^2 + \frac{7}{3}\left(\frac{1\cdot3}{2\cdot4}\right)^2 e^4 - \text{etc.}\right]$$

$$= \pi\sqrt{\frac{2}{\mu}}\, c^{\frac{3}{2}}\left(e^{-\frac{3}{2}}\,\mathrm{f}(e)\right),$$

in which $\mathrm{f}(e)$ is a contraction for the expression in square brackets.

Now since $\lambda = KT$ (T., 1921, **119**, 1656), and since the value of the combined constants can be obtained from a particular case, we get

$$\lambda = \pi K\sqrt{\frac{2}{\mu}}\, a^{\frac{3}{2}}\,\mathrm{f}(e) = 112a^{\frac{3}{2}}\,\mathrm{f}(e) = 112\, c^{\frac{3}{2}}\,(e^{-\frac{3}{2}}\mathrm{f}(e)).$$

The quantity c in the above equation is half the distance between the centres of auxochrome and hapton, and the eccentricity of the ellipse depends on how far out from these centres the electron-orbit passes at the end of its major axis ($2a$ in length). In the case of the very simple compounds the electron must just graze the outer "octet" of the auxochrome and hapton, in which case $2a = 2c + d$, where d is the diameter of the oxygen atom = 1·30 Å. In all simple cases it so happens that $d = 1{\cdot}3$ (or $a = c + 0{\cdot}65$), because the oxygen and nitrogen atoms characteristic of auxochromes both have this diameter.

Simplification of the Eccentricity Function.—The eccentricities of all the ellipses concerned vary only between 0·75 and 0·90. The

complicated expression $f(e) = 1 - \frac{3}{1}\left(\frac{1}{2}\right)^2 e^2 + \text{etc.}$ may therefore be replaced by an approximation easier to work with. I find that the simple expression $f(e) = 1{\cdot}249 - 0{\cdot}79e$ gives results within 2 per cent. of the truth over the range specified.

Calculation of the Position of Absorption Bands. A. Ionised Quinol and p-*Aminophenol.*—Let P be the centre of an oxygen atom and Q the centre of either another oxygen atom or of the nitrogen atom of the amino-group, using a diagram similar to Fig. 5. The distance PQ is greater than in the case of benzene (namely, 3·82 Å.) by an amount proportional to the larger radius of oxygen as compared with hydrogen: $PQ = 3{\cdot}82 + \frac{2}{\sqrt{3}}(0{\cdot}65 - 0{\cdot}50) = 4{\cdot}00$ Å. This is $2c$ in the λ equation; therefore $c = 2{\cdot}00$. The major axis of the ellipse ($2a$) is $4{\cdot}00 + 1{\cdot}30 = 5{\cdot}30$ Å., and $a = 2{\cdot}65$ Å.

Hence the eccentricity is $2{\cdot}00/2{\cdot}65 = 0{\cdot}755$; and $f(e)$ is approximately 0·653.

Hence λ (calc.) $= 112a^{\frac{3}{2}} f(e) = 112 \times (2{\cdot}65)^{\frac{3}{2}} \times 0{\cdot}653 = 315$.

The observed λ of these substances is 315 and 310 respectively.

B. Phenoxide-ion and Aniline.—The length of PQ, when one atom is hydrogen and the other either oxygen or nitrogen, may be shown by trigonometry to be $3{\cdot}91$ Å $= 2c$. An orbit just grazing the outsides of O and H (or N and H) will have a major axis of $3{\cdot}91 + 0{\cdot}65 + 0{\cdot}5 = 5{\cdot}06 = 2a$.

Hence $e = 3{\cdot}91/5{\cdot}06 = 0{\cdot}774$, and $f(e) = 0{\cdot}638$.

The calculation of λ gives $112 \times (2{\cdot}53)^{\frac{3}{2}} \times 0{\cdot}638 = 288$.

The observed λ of phenoxide is 288, and that of aniline 284.

C. Benzene.—The length of PQ is 3·82 Å. $= 2c$. An orbit just grazing two hydrogens would have $2a = 4{\cdot}82$, whence the calculated λ is $112 \times (2{\cdot}41)^{\frac{3}{2}} \times f(e) = 261\frac{1}{2}$.

One of the benzene absorption bands is actually at this place, and it is probable that the other bands correspond each to a distance between hydrogens in the molecule.

D. p-*Hydroxybenzyl Alcohol Ion* (see Fig. 6).—The angle QCM is made equal to 109° 28′, the ordinary tetrahedral angle of carbon. It can be shown that QC is parallel to PN. The perpendicular from P on QC $= 3{\cdot}37$ Å., and $PQ = \sqrt{(3{\cdot}37)^2 + (0{\cdot}84)^2} = 3{\cdot}47$ Å. $= 2c$.

If the orbit just grazes the outsides of the two oxygen atoms, $2a = 3{\cdot}47 + 1{\cdot}3 = 4{\cdot}77$ Å.: the value of e is 0·73 and $f(e) =$ about 0·673. The calculated λ is $112 \times (2{\cdot}385)^{\frac{3}{2}} \times 0{\cdot}673 = 278$. The observed value is 293.

To obtain agreement between theory and observation it may be

assumed that the orbit is slightly deflected by the C_6H_4 and CH_2 groupings lying sideways. An enlargement of the major axis from 2·385 to 2·44 is required to get agreement, which means that the electron passes outside both oxygen atoms at a distance of 0·055 Å. This supposition is not unreasonable, since it is of the same order of magnitude as the loading-effect of an inactive benzene ring, as seen, for example, in the change from Michler's carbinol to malachite green (λλ 603 and 619, respectively).

E. p-*Hydroxybenzaldehyde.*—Using the same diagram as in the preceding case, we suppose the angle QCM now to be 125° 16′, the ordinary angle between *double bonds* in the tetrahedron. QC diverges from PN. The perpendicular = 3·68 Å., and PQ = $2c$ = 3·87 Å. Hence, on the assumption of a grazing orbit, $2a$ = 5·17 Å. Allowing for "loading" as above, the corrected value of $2a$ = 5·28 Å. The calculated λ is 323. The observed λ is 330. It is to be noted that the orbit for *pp′*-dihydroxybenzophenone, $CO(C_6H_4{\cdot}O')_2$, going from central oxygen to phenoxide oxygen is practically identical with that of *p*-hydroxybenzaldehyde. The observed λ is 323, almost the same, and agreeing better with the calculation.

Dicyclic Compounds.

A. Quinhydrone.—When this is formulated as

$$O{:}C_6H_4{:}O(OH){\cdot}C_6H_4{\cdot}OH,$$

the three oxygen atoms are in a straight line and it is obvious that the extreme length is twice that of quinol, or 8·00 Å. = $2c$. There being no "loading," the value of $2a$ for a grazing orbit is 9·3. Hence e = 0·862 and the approximate value of f(e) is 0·570.

The calculated λ is $112 \times (4{\cdot}65)^{\frac{3}{2}} \times 0{\cdot}570 = 645$.

Quinhydrone absorbs the whole of the red end of the spectrum from λ 600 to λ 800 indefinitely. The orbit must therefore have a larger (and more varying) a than the one suggested.

B. Dihydroxybenzhydrol-ion.—Here the central atom is carbon, and the angle between the valencies is 109° 28′ (see Fig. 7). The distance PC in the figure is shown by trigonometry to be 4·065 Å., whence the distance PQ in the figure is 6·64 Å. = $2c$. From the position of the benzene rings there will be "loading" of the orbit, which may be taken to be the same as in the monocyclic series, that is, as indicated by an increase of the major axis by 0·11 Å. Thus $2a = 6{\cdot}64 + 1{\cdot}3 + 0{\cdot}11 = 8{\cdot}05$. Hence f($e$) is about 0·598 and the calculated λ is $112 \times (4{\cdot}025)^{\frac{3}{2}} \times 0{\cdot}598 = 542$ (observed λ = 539).

The same figure serves for diaminobenzhydrol and for aurin: in the former case the orbit would be slightly larger (owing to the hydrogen atoms attached to the nitrogen being outside the orbit);

and in the case of aurin the distances between the three oxygen atoms are equal and the orbit is practically the same as in dihydroxybenzhydrol, *a* and *c* being the same. The observed λ is 550 and 534 in the respective cases.

C. *Indophenol and indamine.*—The diagram for quinhydrone is used, the sizes of central oxygen and nitrogen being the same. The rings, however, lie at an angle to each other. The angle of 133° suggested in T., 1922, **121**, 1812, is too small because of the variation of f(*e*), which was not taken into account in that communication. An angle of 155° to 160° is required for agreement between calculation and observation ($2c = 7{\cdot}85$, $2a = 9{\cdot}26$).

This completes the treatment of the fundamental substances. The investigation of the other effects of loading, required to give a physical basis to the small colour-factors given in T., 1921, **120**, 1661 (bottom) is not justified in our present state of knowledge.

Thus, to account for the colour of Michler's carbinol, malachite-green, and crystal-violet, we require an orbit of which the interfocal distance, 2*c*, is the same as that of dihydroxybenzhydrol, but the major axis is longer in terms of the substitution NMe_2/OH. The required values for 2*a* are 8·42, 8·50 and 8·40 respectively.

It may be well, however, to repeat that since all the monocyclic substances can be expressed as derivatives of *p*-hydroxybenzyl alcohol and quinoneimine, the interfocal distance 2*c* is probably always about 3·47 in fuchsone and its derivatives and the benzhydrol compounds; and about 3·87 in the oxidised compounds connected with *p*-hydroxybenzaldehyde; whilst 2*c* is about 4·00 in the compounds containing nitrogen. In other words, "loading" is due to change of eccentricity of the ellipse, *of which the foci are fixed*. An examination of the experimental data (Moir, T., 1923, **123**, 2796) shows that the position of the absorption bands corresponds to λλ 290 and 360 with various loadings, the former constituting the all-carbon class and the latter the nitrogen-containing class.

Other cases of change of colour seem to depend on change of shape of the benzene ring. Thus quinol (ionised) and *p*-benzoquinone are both $C_6H_4O_2$ and the most likely explanation is that quinone is shaped like a plane (not skew) hexagon. The required distance between the centres of the oxygen atoms is 5·85 Å. (as against 4·00 in ionised quinol). Perhaps the *X*-ray investigators will examine *p*-benzoquinone to test this prediction.

In conclusion, the author expresses the hope that workers in many other fields may be able to make use of the new information regarding the geometry of benzene given in this paper. As an example the structure of diphenyl may be given.

The angle between the tops of the rings is easily shown to be

70° 32′, the same as the angle θ of page 1137, hence since AD = GD = 3·23 Å., AG = 3·74 Å.

Hence the *pp*-position in diphenyl is similar in distance to the *p*-position in benzene. Applying these considerations to the case of benzidine by assuming two nitrogen atoms attached (see Fig. 8), we find that the distance between the centres of the two nitrogen atoms is 3·30 Å., a quantity smaller than the distance between the nitrogen atoms of *p*-phenylenediamine. The formation of insoluble benzidine sulphate is thus easily understood, being analogous to that of barium sulphate. Similarly the distance between the oxygen atoms of 4 : 4′-diphenol is also 3·30 Å. only, so that the formation of diphenoquinone by loss of two very adjacent hydrogen atoms is easily understood.

Note.—At the end of the previous paper (T., 1922, **121**, 1813), the figure 0·926 was given as representing the contraction on replacing two hydrogen atoms by the oxo-linkage. Under the present theory the ratio of the major axes of quinhydrone and phenoxide (the latter taken twice) gives the same datum. This ratio is 9·30 ÷ (2 × 5·06) = 0·920, using the Bragg data. This confirms the idea that the correct sizes of the molecules have been ascertained.

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CXXXV.—*Synthesis of Cyclic Polysulphides. Part I. Condensation of Dithioethylene Glycol with Benzylidene Chloride.*

By SIR PRAFULLA CHANDRA RÂY.

THE two main products of the reaction between dithioethylene glycol (2 mols.) and benzylidene chloride (1 mol.) are *benzylidene diethylene tetrasulphide*, $CHPh<^{S\cdot C_2H_4\cdot S}_{S\cdot C_2H_4\cdot S}$, and *benzylidene diethylene trisulphide*, $CHPh<^{S\cdot C_2H_4}_{S\cdot C_2H_4}>S$, respectively produced by atmospheric oxidation and by loss of hydrogen sulphide (1 mol.) from an unisolable, intermediate compound, $CHPh(S\cdot C_2H_4\cdot SH)_2$. Two by-products, namely, diethylene disulphide and diethylene trisulphide, formed by the intermolecular condensation of the thioglycol itself, have been isolated.

Benzylidene diethylene tetrasulphide is not a "thiol," for it does not decolorise a solution of iodine and on treatment with

mercuric chloride it yields an additive compound instead of a chloromercaptide.

According to the duration of heating, the reaction between benzylidene diethylene trisulphide and boiling methyl iodide yielded substances approximating in composition to the formulæ $C_4H_8S_2$,2MeI and C_4H_8S,3MeI. With ethyl iodide, the definite products isolated were an *ethiodide*, $2C_{11}H_{14}S_2$,EtI, and diethylene di- and tri-sulphides.

Benzylidene diethylene trisulphide, on oxidation with nitric acid, does not yield the corresponding sulphone (compare triethylene trisulphide, J., 1923, **123**, 2174), but is converted into benzoic acid, ethanedisulphonic acid and sulphuric acid. The tri- and tetra-sulphides both yield well-defined double compounds with platinic chloride in which the valency of platinum is variable (compare J., 1923, **123**, 133).

EXPERIMENTAL.

Interaction of Benzylidene Chloride and Dithioethylene Glycol.—Hydrogen chloride and sulphide were evolved when a mixture of 18 grams of the thioglycol and 15 grams of benzylidene chloride was gently boiled for about thirty hours. The heavy oil produced was thoroughly washed with dilute alkali and with water, and repeatedly extracted with hot alcohol. The extract, separated from the insoluble residue (A), was filtered after twelve hours to remove a small, crystalline deposit, the alcohol distilled, and the oily residue washed several times with cold alcohol. A portion dissolved (B), leaving a heavy oil (C). From B, on evaporating the alcohol, *benzylidene diethylene trisulphide* was obtained as an oil, $d_{32°}^{32°}$ 1·189 (Found: C = 54·29; H = 6·03; S = 39·54. $C_{11}H_{14}S_3$ requires C = 54·13; H = 5·80; S = 39·66 per cent.). The oil (C), which contained a trace of a solid, was extracted with ether; the solution, on evaporation, yielded *benzylidene diethylene tetrasulphide* as a golden-yellow, mobile oil (Found: C = 47·79; H = 5·70; S = 46·69. $C_{11}H_{14}S_4$ requires C = 47·83; H = 5·79; S = 46·38 per cent.). The solid residue (A), twice crystallised from benzene, furnished diethylene trisulphide, m. p. 96° (Found: S = 63·21. Calc. 63·16 per cent.), the mother-liquor on concentration yielding diethylene disulphide, m. p. 75°.

Reactions of Benzylidene Diethylene Tri- and Tetra-sulphides with Mercuric Chloride and Platinic Chloride.—These sulphides reacted with mercuric chloride in alcoholic solution to give, the former a white, flocculent precipitate (Found: Hg = 55·55; Cl = 19·15; C = 15·83. $C_9H_{10}S_2$,2$HgCl_2$ requires Hg = 55·25; Cl = 19·60; C = 14·92 per cent.), and the latter, in hot solution, a white,

crystalline precipitate (Found : Hg = 30·63; Cl = 10·45. $C_{11}H_{14}S_4,HgCl_2,2EtOH$ requires Hg = 31·30; Cl = 11·16 per cent.).

These double compounds, and also the following ones with platinic chloride, often contain one or more molecules of ether or alcohol of crystallisation or combination.*

The precipitate obtained from benzylidene diethylene trisulphide and platinic chloride in warm alcohol was washed with alcohol and dried in a vacuum desiccator (Found : Pt = 38·60; Cl = 13·63; C = 25·39; H = 3·44. $C_{11}H_{14}S_3,PtCl_2$ requires Pt = 38·63; Cl = 13·93; C = 25·88; H = 2·76 per cent.). The filtrate on slow evaporation deposited crystals containing sometimes 2 and sometimes 3 mols. of alcohol of crystallisation.

In an alcoholic solution of platinic chloride and benzylidene diethylene tetrasulphide an orange precipitate (A) gradually formed, which was washed with ether (Found : Pt = 25·54; Cl = 14·38. $3C_{11}H_{14}S_4,2PtCl_3,2EtOH$ requires Pt = 25·87; Cl = 14·00 per cent.). From the filtrate, on slow evaporation, two crops of crystals (B and C) were obtained [Found : in (C), Pt = 34·35; Cl = 12·00. $C_{11}H_{14}S_4,PtCl_2,EtOH$ requires Pt = 33·50; Cl = 12·08 per cent. In another preparation, 2 mols of alcohol of crystallisation were found.] B was a mixture of A and C.

Interaction of Benzylidene Diethylene Trisulphide and (a) *Methyl Iodide,* (b) *Ethyl Iodide.*—(*a*) The trisulphide was heated under reflux with excess of methyl iodide for three hours, the excess of the iodide distilled off, the treacle-like product washed with cold alcohol and dissolved in acetone, and the filtered solution precipitated by ether (Found : C = 18·76; H = 3·69; S = 16·61; I = 61·76. $C_4H_8S_2,2MeI$ requires C = 17·82; H = 3·49; S = 15·84; I = 62·86 per cent.).

In a similar reaction lasting twelve hours, the semi-solid mass obtained was extracted with water, the aqueous solution concentrated to small bulk and treated with alcohol, when a white substance, m. p. 212° (decomp.) crystallised (Found : C = 16·41; I = 72·00; S = 6·54. $C_4H_8S,3MeI,\frac{1}{2}H_2O$ requires C = 16·02; I = 72·80; S = 6·12 per cent.).

(*b*) The trisulphide was heated under reflux with ethyl iodide for two hours, the excess of the iodide evaporated, the viscous oil well washed with cold alcohol, and the residual oil dried in a vacuum (Found : I = 20·66; S = 30·60. $2C_{11}H_{14}S_2,EtI$ requires I = 19·84; S = 30·00 per cent.). The mixture of white solid and viscous oil obtained by slow evaporation of the alcoholic washings was dissolved in hot benzene, and, on cooling, diethylene trisulphide,

* Some of these compounds are crystalline, whilst others are granular in structure; hence the term *ether or alcohol of crystallisation or combination.*

m. p. 96°, crystallised. Treatment of the cold, concentrated benzene filtrate with alcohol yielded diethylene disulphide. The final filtrate on evaporation furnished an oil (Found: C = 54·25; H = 3·72; S = 42·31. $C_7H_6S_2$ requires C = 54·54; H = 3·90; S = 41·56 per cent.), which might have been benzylidene disulphide, $C_6H_5 \cdot CHS_2$. Unfortunately, the quantity obtained was barely sufficient for purposes of analysis.

Oxidation of Benzylidene Diethylene Trisulphide with Nitric Acid.—The trisulphide was heated in a sealed tube with fuming nitric acid for one hour at 100°, the excess of nitric acid evaporated, the viscous residue, diluted with a little water, was filtered from the precipitate of benzoic acid, neutralised with barium carbonate, the barium sulphate removed, and the filtrate concentrated, when barium ethanedisulphonate slowly crystallised (Found: Ba = 40·97; S = 20·75. Calc., Ba = 41·02; S = 19·16 per cent.).

In conclusion, I wish to express my warm thanks to Mr. Kshitish Chandra Rây for his ungrudging help in connexion with the experimental part of the work.

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CXXXVI.—*Formation of 3-Halogenocarbazoles from Carbazole-3-diazonium Halides.*

By STANLEY HORWOOD TUCKER.

THE isolation of carbazole-3-diazonium chloride in a crystalline condition (Morgan and Read, J., 1922, **121**, 2711, and by the author) has made it possible, by treating its acetone solution with copper, to prepare 3-chlorocarbazole from it (compare Schwalbe and Wolff, *Ber.*, 1911, **44**, 234; J., 1911, **99**, 103; and the corresponding negative result with tetrahydrocarbazole derivatives mentioned by Edwards and Plant, J., 1923, **123**, 2395). The position of the chlorine atom in the latter is thus proved, for the constitution of carbazole-3-diazonium chloride is established, since it is derived from 3-aminocarbazole, synthesised by Nietzki (*Ber.*, 1895, **28**, 297). Further confirmation is afforded by the independent synthesis accomplished by Ullmann (*Annalen*, 1904, **332**, 93, 95).

Carbazole-3-diazonium bromide and iodide can be obtained as yellow, crystalline precipitates by adding an aqueous solution of carbazole-3-diazonium chloride to aqueous solutions of potassium bromide and iodide, respectively. Carbazole-3-diazonium bromide

can be converted into 3-bromocarbazole by treatment of its methyl ethyl ketone solution with copper. Carbazole-3-diazonium iodide, by simple solution in acetone, decomposes, giving 3-iodocarbazole. The yields in the preparation of 3-chloro- and 3-bromo-carbazole are small, since carbazole also is produced, but the latter can be removed by acetylation of the mixture, followed by hydrolysis—a method which is of especial value in the carbazole series.

When carbazole-3-diazonium bromide is heated with acetic anhydride containing a trace of concentrated sulphuric acid, it undergoes transformation into 3-acetoxy-*N*-acetylcarbazole (Ruff and Stein, *Ber.*, 1901, **34**, 1668).

The work herein described was instituted to establish the constitution of 3-iodocarbazole obtained by direct iodination of carbazole, by a process to be published shortly; 3-iodocarbazole being required for synthesis of the dicarbazyls.

Experimental.

Carbazole-3-diazonium chloride, obtained by a process similar to that of Morgan and Read (*loc. cit.*), was several times recrystallised by dissolving it in water at about 40° and cooling to 0°. After drying in the cold for 24 hours, these crystals softened at 63° and gave a clear yellow, effervescing melt at 100°. The diazo-nitrogen was estimated by heating the substance in nitrobenzene or, better, in acetic anhydride in an atmosphere of carbon dioxide, collecting and measuring the nitrogen evolved (Found: diazo-N_2 = 9·8; Cl = 12·6. $C_{12}H_8N_3Cl,3H_2O$ requires diazo-N_2 = 9·9; Cl = 12·5 per cent.). Crystals of carbazole-3-diazonium chloride containing $3H_2O$, on being kept in a warm room, rapidly changed to the dihydrate, an orange powder (Morgan and Read, *loc. cit.*), and both forms, when exposed in a vacuum over concentrated sulphuric acid, slowly gave the anhydrous carbazole-3-diazonium chloride, an orange-yellow, extremely hygroscopic powder.

Hydrated carbazole-3-diazonium chloride, when pure, dissolves in methyl, ethyl, or amyl alcohol, glacial acetic acid, or acetic anhydride to give clear yellow or light brown solutions which gradually turn deep green when boiled. Acetone and methyl ethyl ketone dissolve it to give yellow solutions which are inappreciably affected by boiling. Pyridine, and bases generally, give scarlet solutions.

3-*Chlorocarbazole*.—Carbazole-3-diazonium chloride dihydrate (5 grams) was dissolved in acetone (50 c.c.) and copper-bronze added. The separated solution was poured into water, and the green precipitate extracted with carbon tetrachloride. The dilute carbon tetrachloride solution deposited a yellow product con-

taining carbazole. It was separated, the filtrate evaporated, and the residue (1 gram) boiled for a few minutes with acetic anhydride containing a trace of concentrated sulphuric acid. The crystals which separated on cooling were recrystallised from dilute acetic acid, and melted at 124°, with slight sign of change at 120° (compare Mazzara and Lamberti-Zanardi, *Gazzetta*, 1896, **26**, ii, 239; and Stevens and Tucker, J., 1923, **123**, 2145). This substance, 3-chloro-*N*-acetylcarbazole, was hydrolysed by dilute alcoholic potassium hydroxide solution; the product crystallised from glacial acetic acid, and then from alcohol, in thick plates, which melted at 195°, alone or mixed with a specimen of 3-chlorocarbazole prepared by Ullmann's method (*loc. cit.*) (Found: Cl = 17·5. Calc., Cl = 17·6 per cent. Compare Mazzara and Lamberti-Zanardi, *loc. cit.*, p. 238).

Carbazole-3-diazonium bromide was prepared by (i) treating 3-aminocarbazole (15 grams), dissolved in 12 per cent. hydrobromic acid (200 c.c.) and water (200 c.c.), with aqueous sodium nitrite (5·7 grams) at about 15°; the filtered solution, cooled in ice, deposited small, yellow needles (pure, recrystallised product, 10 grams); (ii) cooling to 0° a mixture of warm aqueous carbazole-3-diazonium chloride and cold aqueous potassium bromide; the yellow, crystalline precipitate which separated was recrystallised by cooling the filtered solution in warm water with ice. It turns faintly green at 95° and melts with decomposition at 110°. Carbazole-3-diazonium bromide is less soluble in water than the chloride; but since its solution is more stable at higher temperatures, purification by crystallisation from water is easily accomplished. The estimation of diazo-nitrogen was performed by heating in acetic anhydride (Found: Br = 25·6; diazo-N_2 = 9·3. $C_{12}H_8N_3Br,2H_2O$ requires Br = 25·8; diazo-N_2 = 9·0 per cent.). Carbazole-3-diazonium bromide dissolves without decomposition in boiling acetone, methyl ethyl ketone, or methyl or ethyl alcohol. It is slightly soluble in ethyl acetate. It dissolves in amyl alcohol with production of a dark green solution which finally turns brown; in nitrobenzene, acetic anhydride, and pyridine to dark red solutions; and in *cyclo*hexanone to a deep red-violet solution which soon turns brown. The coloured solutions evolve nitrogen when boiled. Carbazole-3-diazonium bromide loses its water of crystallisation when exposed in a vacuum over concentrated sulphuric acid.

3-*Bromocarbazole*.—Carbazole-3-diazonium bromide dihydrate (7 grams) was mixed with methyl ethyl ketone (50 c.c.) and copper-bronze added. The subsequent treatment was the same as in the preparation of 3-chlorocarbazole. The acetylated product was boiled in alcoholic solution with animal charcoal, and recrystal-

lised from alcohol, pyridine, and benzene, in succession, to give stellar clusters of colourless needles, m. p. 127° (compare Ciamician and Silber, *Gazzetta*, 1882, **12**, 276). This 3-bromo-*N*-acetylcarbazole was hydrolysed, and the product recrystallised from alcohol. It was obtained in white, nacreous plates, m. p. 194—195°, and was identical with a specimen prepared by Ciamician and Silber's method (*loc. cit.*) (Found: Br = 32·3. Calc., Br = 32·5 per cent.). Compare also Vaubel (*Z. angew. Chem.*, 1901, **14**, 784) and Mazzara and Leonardi (*Gazzetta*, 1892, **22**, ii, 571, footnote).

3-*Acetoxy*-N-*acetylcarbazole*.—A solution of carbazole-3-diazonium bromide in acetic anhydride was boiled until effervescence had ceased; a few drops of concentrated sulphuric acid were added and the boiling continued for 20 minutes. The product was treated with water, the brown precipitate dissolved in excess of alcohol, and the solution boiled with animal charcoal. The filtered solution was faintly yellow, and slowly deposited stellar clusters of white needles. After several crystallisations from alcohol, colourless rods, m. p. 112—113°, were obtained (Found: C = 71·8; H = 5·0. Calc. for $C_{16}H_{13}O_3N$, C = 71·9; H = 4·9 per cent.). The substance is therefore identical with 3-acetoxy-*N*-acetylcarbazole isolated by Ruff and Stein (*loc. cit.*).

Carbazole-3-diazonium iodide was precipitated as a canary-yellow, crystalline product on the addition of a solution of carbazole-3-diazonium chloride in water to an aqueous solution of potassium iodide; there was no evolution of nitrogen. The carbazole-3-diazonium iodide was separated and washed with cold water, in which it was only slightly soluble. It could not be recrystallised, since it decomposed, with evolution of nitrogen, in all solvents. The water-washed material was dried in the air, and found to contain 1 mol. of water of crystallisation. It became green at 73° and decomposed explosively at 81° (Found: diazo-N_2 = 8·3; I = 37·5. $C_{12}H_8N_3I,H_2O$ requires diazo-N_2 = 8·3; I = 37·5 per cent.). Carbazole-3-diazonium iodide decomposes very slowly, turning green, a change rapidly effected in the light, and the nitrogen value falls. It gives a red compound when treated with ammonia. It dissolves in aniline and pyridine to form scarlet solutions; in chloroform and amyl alcohol to green solutions; in methyl and ethyl alcohols, acetone, glacial acetic acid, and ethyl acetate to faintly brown solutions containing free iodine; and in acetic anhydride to a solution which, on addition of a trace of concentrated sulphuric acid, turns an intense sea-blue, and, on warming, a brilliant brick-red. It is practically insoluble in dichloroethylene and slightly soluble in ether and in light petroleum.

3-Iodocarbazole.—Carbazole-3-diazonium iodide was added to acetone in the cold. Immediately liberation of nitrogen commenced, the mixture became warm, decomposition proceeded vigorously, and finally a brown solution containing free iodine was obtained. The acetone was evaporated and the brown, crystalline residue, containing a trace of lachrymatory substance, dissolved in alcohol, from which, after boiling with animal charcoal and cooling, there separated colourless plates; it may also be crystallised from carbon tetrachloride, in which it is much less soluble. The resulting crystals are nacreous plates which give a colourless melt at 192—194° (Found: I = 43·4. $C_{12}H_8NI$ requires I = 43·3 per cent.).

The above decomposition can also be brought about by warming the ethyl acetate, alcohol, or glacial acetic acid solution of carbazole-3-diazonium iodide. With the last two solvents, green products are obtained, especially if the diazonium iodide is slightly impure.

3-Iodo-N-acetylcarbazole was prepared by boiling, for 1 minute, a solution of 3-iodocarbazole in acetic anhydride containing a trace of concentrated sulphuric acid. It separated from the boiling solution, and crystallised from alcohol in needles, m. p. 145—147° (Found: I = 37·9. $C_{14}H_{10}ONI$ requires I = 37·9 per cent.).

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CXXXVII.—*Application of Thallium Compounds in Organic Chemistry. Part I. Thallous Hydroxide.*

By ROBERT CHARLES MENZIES and EDWARD MANWARING WILKINS.

THALLIUM is not a rare element and it is probable that its compounds would have more general application for research purposes if the ease with which they can be prepared and crystallised were more commonly realised (see Freudenburg and Uthemann, *Ber.*, 1919, **52**, 1509). For more than 2 years one of us (R. C. M.) has habitually used as a laboratory reagent aqueous thallous hydroxide solutions prepared by double decomposition of thallous sulphate and baryta (Lamy, *Ann. Chim. Phys.*, 1863, [iii], **67**, 392). The high equivalent weight of the metal, the convenient solubilities of most organic thallous salts, the insolubility of the iodide, and the ready solubility of the hydroxide in water with formation of a strongly alkaline solution constitute a standard solution of the latter a reagent by means of which almost any acid may be titrated with simultaneous formation of a readily analysed salt; a suitable indicator is phenolphthalein, which should be added to the (organic)

acid, as the red colour is slowly discharged by moderately concentrated aqueous solutions of thallous hydroxide, especially on warming. The well-known strongly alkaline nature of the latter is also shown by its dissolving isatin to form a deep purple liquid the colour of which on warming with slight excess of the reagent changes to yellow. As in the case of alkaline hydroxides, this is due to the formation of a salt of isatic acid, for after concentration *thallous isatate* separates out on cooling in clusters of yellow needles, decomp. 148° (Found : Tl = 55·2. $C_8H_6O_3NTl$ requires Tl = 55·4 per cent.). Thallous salts are generally isomorphous with the salts of the alkali metals (Thorpe, J., 1876, i, 859), and in cases where the excessive solubility of the latter makes their isolation and purification difficult, the more sparingly soluble thallous salts are often much easier to prepare. Thus the yellow potassium salt of salicylaldehyde is exceedingly soluble in water (Rivals, *Ann. Chim. Phys.*, 1897, [vii], **12**, 557), but the corresponding thallous salt readily crystallises from a solution of salicylaldehyde in an equivalent amount of 10 per cent. (0·453*N*) aqueous thallous hydroxide in yellow needles, m. p. 186° (decomp.) after recrystallisation from alcohol, in which it is sparingly soluble (Found : Tl = 63·25. $C_7H_5O_2Tl$ requires Tl = 62·8 per cent.).

Thallous Salts of Mono- and Di-basic Normal Aliphatic Acids.—The valerate, shortly described by Kuhlmann (*Annalen*, 1863, **126**, 78), was prepared by adding thallous hydroxide solution to valeric acid until the reaction was faintly alkaline to litmus, evaporating the solvent, and recrystallising the residue from benzene. The salt, m. p. 145—147°, is very soluble in water, ethyl alcohol, or hot benzene, readily soluble in amyl alcohol, and sparingly soluble in boiling ether, hot light petroleum, or cold benzene; it is not readily thrown out of solution in ethyl alcohol by addition of ether (Found : in a sample dried for 2 hours at 130°, Tl = 67·1. $C_5H_9O_2Tl$ requires Tl = 66·9 per cent.).

The *palmitate*, prepared by adding 33 per cent. thallous hydroxide solution to a hot alcoholic solution of palmitic acid until the reaction was neutral to litmus, crystallised from alcohol in feathery aggregates. It is readily soluble in hot alcohol, insoluble in ether, and soluble in water, the solution being opalescent when dilute. On shaking a warm dilute aqueous solution, a froth forms on the surface, which disappears on cooling, and is not formed on shaking the cold solution (Found : in the salt dried in air at 100°, Tl = 44·15. $C_{16}H_{31}O_2Tl$ requires Tl = 44·4 per cent.). It softens on heating at 116—118°, but does not melt completely at 170°.

The *oleate* was prepared by adding the theoretical amount (11 c.c. of 0·804*N*) of thallous hydroxide solution to 2·5 grams of oleic acid,

dissolved in alcohol, and evaporating the solution to dryness in a vacuum desiccator. The residual soap separated from ethereal solution in white needles, which were soft and could easily be bent; on drying, they cohered to a solid, soap-like mass. The salt is also soluble in perfectly dry ether free from alcohol. A sample of thallous oleate which had been kept for some months in a corked tube, and had become superficially blackened, was boiled with water. The dark colour was discharged, and an opalescent solution was obtained which gave, on shaking, a froth permanent in the cold (distinction from the palmitate). Part of the oleate did not dissolve: twenty-four hours later, this was found to have formed a jelly below the main bulk of the solution, the volume of the jelly being many times greater than that of the oleate left undissolved the previous day. For analysis, the salt was recrystallised from ether and dried in a vacuum desiccator for a month (Found: Tl = 41·3. $C_{18}H_{33}O_2Tl$ requires Tl = 42·0 per cent.).

The normal *adipate* was prepared by accurately neutralising 3·2 grams of adipic acid with aqueous thallous hydroxide solution (0·453*N*), using phenolphthalein as indicator. The solution was evaporated to small bulk and the crude adipate precipitated with ethyl alcohol, 8 grams being obtained in the first instance, and a further 1·5 grams from the filtrate (a yield of 78 per cent.). The salt was dissolved in ethylene glycol, in which it is very soluble, and butyl alcohol added with continued heating until a faint cloudiness was apparent in the boiling mixture; on cooling, the salt separated out in crystalline leaflets, which were dried at 100° (Found: Tl = 73·3. $C_6H_8O_4Tl_2$ requires Tl = 73·9 per cent.).

The normal *pimelate* was obtained by neutralising 0·804 gram of pimelic acid in 100 c.c. of water with thallous hydroxide solution of unknown strength (29·85 c.c.; see acid salt below), using phenolphthalein as indicator, and evaporating the solution to dryness. It is much more soluble in water than the normal adipate, and is almost insoluble in ethyl alcohol, but can be recrystallised from amyl alcohol, in which at the boiling point it is sparingly soluble, separating on cooling in long needles (Found: in material dried for 2 hours at 100°, Tl = 71·8. $C_7H_{10}O_4Tl_2$ requires Tl = 72·1 per cent.).

The *acid pimelate* was prepared as follows. To a further 100 c.c. of the above solution of pimelic acid were added 15 c.c. of the same thallous hydroxide solution as was used for the preparation of the normal salt; on evaporation of the solution, acid thallous pimelate was obtained. It is readily soluble in water, almost insoluble in ethyl alcohol, and crystallises from amyl alcohol in prisms. For

analysis, it was recrystallised from butyl alcohol. M. p. 137—140° (Found : Tl = 55·9. $C_7H_{11}O_4Tl$ requires Tl = 56·2 per cent.).

Thallous Salt of Ethyl Acetonedicarboxylate.—The minute needles obtained when cold 10 per cent. thallous hydroxide solution was shaken with a few drops of acetonedicarboxylic ester were recrystallised from alcohol. The salt melted at 125° (decomp.). Heated at 110°, it lost 31·7 per cent. of its weight, leaving a black residue. For analysis, it was therefore dried in a vacuum desiccator at room temperature (Found : Tl = 49·7. $C_9H_{13}O_5Tl$ requires Tl = 50·4 per cent.). It is readily soluble in cold ethyl or methyl iodide, thallous iodide being deposited on standing or on heating. This property is shared by thallous acetylacetone (Kurowski, *Ber.*, 1910, **43**, 1078; Morgan and Moss, J., 1914, **105**, 195), which can also be prepared in a manner similar to that described above, the thallous hydroxide solution being preferably of a higher concentration.

Qualitative Reactions of Aqueous Thallous Hydroxide Solutions with Sugars (compare Bottger, *Ding. Poly. J.*, 1870, **197**, 379; Freudenberg and Uthemann, *loc. cit.*).—In concentrated aqueous solution, fructose, glucose, and xylose give with 1·5*N*-aqueous thallous hydroxide in the cold yellow precipitates which, on heating, become reddish-yellow, and finally very dark; under suitable conditions mirrors are formed. With 0·453*N*-thallous hydroxide, no precipitates are formed with glucose and fructose, but the same colour changes are observed on heating, and again on heating thallium mirrors are formed, provided only the thallous hydroxide is present in sufficient excess. Sucrose and mannitol can be boiled with 10 per cent. thallous hydroxide solution without change other than the appearance of a faint yellow colour, but on hydrolysis of sucrose with dilute sulphuric acid mirrors are formed on subsequent heating with thallous hydroxide solution. The formation of mirrors is favoured by addition of ammonium or sodium hydroxide. Good results are obtained by heating a mixture of 2 c.c. of *N*-glucose and 5 c.c. of 10 per cent. thallous hydroxide with addition of four or five drops of *N*-sodium hydroxide solution in a clean test-tube at 100° for 2 minutes in a water-bath. The mirrors obtained can readily be removed from the glass by boiling with tap-water, but are permanent for some weeks under cold, air-free, distilled water, as recommended by Bottger for the metal (*loc. cit.*).

On adding tetramethyl γ-fructose to thallous hydroxide solution, a brown colour is developed in the cold, a small amount of a dark, flocculent precipitate being also formed; on boiling, this brown colour becomes darker and the precipitate dissolves. No mirror is formed.

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THE UNIVERSITIES OF ST ANDREWS AND BRISTOL. [*Received, February 4th,* 1924.]

CXXXVIII.—*Derivatives of Semioxamazide. Part II.*

By FORSYTH JAMES WILSON and ERIC CHARLES PICKERING.

IN addition to the ketonic semioxamazones described in Part I. (J., 1923, **123**, 394), we have now obtained *methyl* n-*hexyl ketone semioxamazone*, *dibenzyl ketone semioxamazone* (in two dimorphic forms; dibenzyl ketone semicarbazone also is described in the literature as occurring in two modifications [Wedekind, *Ber.*, 1901, **34**, 2076; Senderens, *Compt. rend.*, 1910, **150**, 1337]), *benzil monosemioxamazone* and *disemioxamazone*, iodine being again employed as catalyst. We were unsuccessful in obtaining semioxamazones of the following ketones: methyl *tert.*-butyl ketone, phenyl styryl ketone, camphor, fructose.

The action of amines upon semioxamazide and semioxamazones was next investigated. It was found that, whilst aniline and dibenzyl ketone semioxamazone did not react on heating for ½ hour at 190°, benzylamine and semioxamazide reacted on heating for 2 hours at 175—180°, giving *s*-dibenzyloxamide, hydrazine, and ammonia in accordance with the scheme $NH_2{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2 + 2CH_2Ph{\cdot}NH_2 = CH_2Ph{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CH_2Ph + NH_3 + N_2H_4$.

Benzylamine and acetophenonesemioxamazone on heating at 150° gave ammonia, *s*-dibenzyloxamide, methyl phenyl ketazine, and hydrazine—$2CPhMe{:}N{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2 + 4CH_2Ph{\cdot}NH_2 = 2CH_2Ph{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CH_2Ph + CPhMe{:}N{\cdot}N{:}CMePh + N_2H_4 + 2NH_3$.

Dibenzyl ketone semioxamazone and benzylamine reacted in a similar manner.

Piperidine and acetophenonesemioxamazone reacted in an entirely different manner, the products obtained by heating these two substances together being ammonia and *acetophenonepiperidino-oxalylhydrazone* — $CPhMe{:}N{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2 + C_5H_{10}NH = CPhMe{:}N{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NC_5H_{10} + NH_3$; the reaction was therefore quite similar to the one which occurs between semicarbazones and primary amines as described by Borsche and his collaborators (*Ber.*, 1901, **34**, 4299; 1904, **37**, 3177; 1905, **38**, 831).

From this hydrazone, by hydrolysis, *piperidino-oxalylhydrazine*, $NH_2{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NC_5H_{10}$, was obtained. The constitution of this hydrazine was shown by its synthesis from ethyl piperidino-oxalate and hydrazine hydrate, $C_5H_{10}N{\cdot}CO{\cdot}CO_2Et + NH_2{\cdot}NH_2 = C_5H_{10}N{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NH_2 + EtOH$, which was effected by heating the reactants in alcoholic solution. The two preparations were identical and gave the same benzylidene derivative. Semioxamazide itself did not react with piperidine on heating.

These investigations will be continued.

EXPERIMENTAL.

Methyl n-*hexyl ketone semioxamazone*,

$$C_6H_{13}{\cdot}CMe{:}N{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2,$$

was prepared by boiling 2 grams of semioxamazide with 3 grams of the ketone in 25 grams of absolute alcohol. On addition of a few crystals of iodine, the semioxamazide dissolved completely within 5 minutes and on cooling the semioxamazone was deposited in the pure condition as small, colourless needles, m. p. 115—116°. The substance was very readily hydrolysed, but could be recrystallised from absolute alcohol (Found : N = 19·8. $C_{10}H_{19}O_2N_3$ requires N = 19·7 per cent.).

Benzil monosemioxamazone, $PhCO{\cdot}CPh{:}N{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2$, was obtained by boiling 0·5 gram of semioxamazide with 3 grams of benzil in 30 grams of absolute alcohol with addition of a little iodine, which effected complete solution in an hour; without addition of iodine there was no indication of any reaction. On cooling, the semioxamazone separated in long, colourless prisms which after recrystallisation from alcohol melted at 181—182° (Found : N = 14·2. $C_{16}H_{13}O_3N_3$ requires N = 14·2 per cent.).

The *disemioxamazone*, $(CPh)_2{:}(N{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2)_2$, which could not be obtained pure, was prepared in the usual way, using excess of semioxamazide and boiling for 4 hours. As it was insoluble in alcohol and in solvents generally, it was purified by extraction with hot acetone to remove excess of semioxamazide, and then with hot alcohol; the disemioxamazone formed a white powder, m. p. 275—278° (decomp.) (Found : N = 21·2, 21·6. $C_{18}H_{16}O_4N_6$ requires N = 22·1 per cent.).

Dibenzyl ketone semioxamazone, $C(CH_2Ph)_2{:}N{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH_2$, which was prepared in the usual way, was found to be dimorphic. From a hot concentrated alcoholic solution colourless prisms melting at 195—196° were deposited at temperatures above 40°, whilst at temperatures below this and from more dilute solutions the semioxamazone crystallised in colourless needles, m. p. 187—189°. A mixture of the two forms softened at 187° and

melted at 194—196° (Found: prisms, N = 14·3; needles, N = 14·5. $C_{17}H_{17}O_2N_3$ requires N = 14·2 per cent.).

Action of Amines.

In the following cases, the reactants, the amine being in excess, were heated until dissolution was effected, ammonia being evolved, and the mixture was then cooled and treated as described.

Benzylamine and *Semioxamazide.*—After 2 hours' heating at 175—180° and cooling, the reaction mixture was treated with a little alcohol which caused an immediate separation of a white powder; this, after recrystallisation from alcohol, was identified as *s*-dibenzyloxamide by comparison with an authentic specimen and by analysis (Found: N = 10·6, 10·6. Calc., N = 10·5 per cent.). The liquid remaining after removal of the dibenzyloxamide was distilled; the distillate reduced silver nitrate in the cold, indicating the presence of hydrazine.

Benzylamine and *Dibenzyl Ketone Semioxamazone.*—After 3 hours' heating at 150° and cooling, ether was added, and the solid that separated was identified as *s*-dibenzyloxamide. The filtrate was freed from ether by distillation and a portion was distilled; hydrazine was identified in the distillate by its reducing action on silver nitrate and on Fehling's solution. The remainder was poured into ice-cold dilute acetic acid; a solid separated, part of which dissolved in ether, the insoluble portion being dibenzyloxamide. The ethereal solution was evaporated and the residue recrystallised from alcohol, which deposited small, colourless prisms of *dibenzylketazine*, m. p. 95—96°: the melting point was not altered by addition of some of the ketazine prepared by the method described below. This ketazine, which does not seem to have been previously prepared, was also obtained by heating 7 grams of dibenzyl ketone with 1·5 grams of hydrazine hydrate in a sealed tube at 100° for 12 hours. Alcohol was then added: after cooling and stirring, a solid separated which after recrystallisation from alcohol formed small, colourless prisms, m. p. 95—96° (Found: N = 6·7. $C_{30}H_{28}N_4$ requires N = 6·7 per cent.).

Benzylamine and *Acetophenonesemioxamazone.*—After 1½ hours' heating at 155—160° and cooling, a little alcohol was added, the dibenzyloxamide that separated was removed, the filtrate poured into ice-cold dilute acetic acid, and the yellow precipitate freed from dibenzyloxamide by extraction with ether and filtering. The ether was evaporated and the residue recrystallised from alcohol, from which yellow needles of methyl

phenyl ketazine, m. p. 129—130°, were deposited (Found : N = 11·9. Calc., N = 11·9 per cent.). The melting point of this ketazine is variously given in the literature as 121° or 127—128°. A specimen prepared by Curtius and Thun's method (*J. pr. Chem.*, 1891, [ii], **44**, 167) melted at 129—130°; a mixed melting point of the two specimens showed no depression.

Piperidine and *Acetophenonesemioxamazone.*—Three grams of the semioxamazone and 5 grams of piperidine were boiled under reflux for 4½ hours, when solution, accompanied by evolution of ammonia, was complete. After cooling, 10 c.c. of alcohol were added, when 2 grams of a solid separated which, repeatedly crystallised from alcohol, yielded *acetophenone piperidinooxalylhydrazone* as a white, microcrystalline powder, m. p. 174—175° (Found : N = 14·7, 14·8. $C_{15}H_{19}O_2N_3$ requires N = 15·0 per cent.). The mother-liquors on evaporation to dryness under reduced pressure gave an oil which solidified on the addition of a little alcohol; this solid, the amount of which was small, melted at 145—155° and was not obtained pure.

A mixture of 4 grams of this hydrazone, 10 c.c. of water, and 5 c.c. of *N*/10-hydrochloric acid was distilled in steam as long as acetophenone passed over, and after being made just alkaline with sodium carbonate, was evaporated to dryness under reduced pressure. The viscous oil remaining was extracted with absolute alcohol, the solvent evaporated, and the residue, which solidified on keeping in a vacuum over sulphuric acid, recrystallised from a mixture of benzene and light petroleum, colourless, transparent plates of *piperidinooxalylhydrazine*, m. p. 77—79°, being obtained (Found : N = 24·4. $C_7H_{13}O_2N_3$ requires N = 24·5 per cent.). The *hydrochloride*, obtained as a white powder from hydrogen chloride and the base in a benzene solution, melted with decomposition at 180° (Found : Cl = 17·5. $C_7H_{14}O_2N_3Cl$ requires Cl = 17·1 per cent.). The *benzylidene* derivative was prepared by warming an alcoholic solution of 2 grams of the hydrazine and 1 gram of benzaldehyde for 2 minutes. On cooling, colourless needles separated which after recrystallisation from alcohol melted at 201—202° (Found : N = 16·3. $C_{14}H_{17}O_2N_3$ requires N = 16·2 per cent.).

The synthesis of piperidino-oxalylhydrazine was effected by gently boiling molecular quantities of ethyl piperidinooxalate and hydrazine hydrate in alcoholic solution for about an hour. Oxalyldihydrazide was precipitated as a by-product. The filtrate was evaporated and the residue solidified on keeping in a vacuum over sulphuric acid. Recrystallisation from a mixture of benzene and light petroleum gave a specimen of the hydrazine

identical with the one just described. The benzylidene derivatives also were identical.

We wish to thank the Carnegie Trust for the Universities of Scotland for a grant which has partly defrayed the expenses of this investigation.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW. [*Received, February 18th*, 1924.]

CXXXIX.—*An Examination of the Binary System Sodium Sulphite–Water by Extrapolation from the Ternary System Sulphite–Sulphate–Water.*

By NEIL BANNATYNE LEWIS and ALBERT CHERBURY DAVID RIVETT.

IN a description of isotherms at 0°, 17·5°, 25°, and 37·5° in the ternary system sodium sulphite–sodium sulphate–water (*Rec. trav. chim.*, 1923, **42**, 954), the authors pointed out, *inter alia*, that at 25° the stable solid phases at the sulphite end of the system were mixed crystals of the heptahydrates of the two salts. Anhydrous solids, also mixed crystals, were obtainable in the same region, but the equilibria between them and their saturated solutions were metastable. This result was unexpected in view of the work of Hartley and Barrett (J., 1909, **95**, 1178), which fixed the transition point of anhydrous and heptahydrated sodium sulphite at about 22°. In their measurements, very pure sulphite was used, prepared by the action of sulphur dioxide on sodium carbonate solutions in absence of oxygen. Evidently some new factor enters when sulphate is present, and it becomes of some interest to examine the binary system to which one is led by extrapolation from the ternary.

That the case is not simple is indicated by an earlier conclusion of Meyerhoffer (Landolt-Börnstein, "Tabellen," 3rd ed., p. 560), based on solubility figures of Mitscherlich (*Pogg. Ann.*, 1827, **12**, 140), that the transition temperature is probably 33°, or 11° above the value established by Hartley and Barrett: later (*op. cit.*, 4th ed.) this was assumed to be a metastable point.

In our first experiments, aiming at determining the solubilities of sodium sulphite in solutions containing up to 10 per cent. of sodium sulphate, we obtained consistent results over a certain temperature range, but quite irregular figures above it. The procedure adopted was the following. Suitable complexes were

prepared from water, excess sodium sulphite heptahydrate crystals, and varying amounts of sodium sulphate, added either as anhydrous salt or decahydrate. The mixture, in a sealed or well-stoppered glass tube, was sometimes pre-heated, and sometimes not, before being rotated in a thermostat at a chosen temperature. Rotation was continued for from 5 to more than 100 hours in different cases. Solid of some sort was always present in those tubes in which anhydrous salt was finally obtained, the temperature coefficient of its solubility making it impossible to obtain a homogeneous complex which would crystallise sufficiently on change of temperature. In analysing solutions, tubes were opened after settlement of solids, and about 5 c.c. quickly withdrawn by means of a pipette carrying a cotton-wool filter, run into a tared flask containing excess of $N/2$-iodine solution, and weighed. The iodine unacted upon was back-titrated with $N/10$-thiosulphate and the weight percentage of sulphite calculated. Into a second tared flask, empty, 10 c.c., similarly withdrawn, were run and weighed. To this, sufficient 10-volume hydrogen peroxide was added to oxidise all sulphite to sulphate, the whole being then evaporated to dryness and weighed. The sulphate originally present, together with the equivalent of the sulphite, was thus obtained as anhydrous salt. It was necessary to treat the peroxide first with barium carbonate to neutralise acid, and on the clear filtered solution, which was used as indicated, to make a determination of the solid left on evaporation. This meant a correction in the weighing of sulphate, usually amounting to about 1 mg. for each c.c. of peroxide solution used. The sulphate content of the solution was at once calculable as a difference. Approximate densities (D_4^{25}) were obtained by comparing the weights withdrawn with the volumes of the pipettes used. They are correct only within 2 or 3 units in the third decimal place.

Quite satisfactory and consistent results were obtained at all temperatures at which the solid phases consisted of hydrated crystals, but in the equilibria where anhydrous salt was formed, the most unexpected irregularities appeared, points being obtained which showed no simple relation at all between solubility of sulphite and the amount of sulphate present. These irregularities, however, were no longer apparent when excess commercial anhydrous sodium sulphite (B.D.H.), which always contains sulphate, was used instead of the hydrated crystals. It was added, with sulphate, to warmed water, and the complex raised to 70° or 80° before being cooled to a suitable lower temperature by rotation in a thermostat. Usually the mixture was seeded, after an hour or more, with hydrated and with anhydrous sulphite.

In all cases up to 31·5° the resulting solids have been large, clear, hydrated, mixed crystals. Above this the stable solids have again been mixed crystals, but anhydrous: metastable hydrates have also been obtained at 35°. A precise examination of the solids is unnecessary for the present purpose.

FIG. 1.

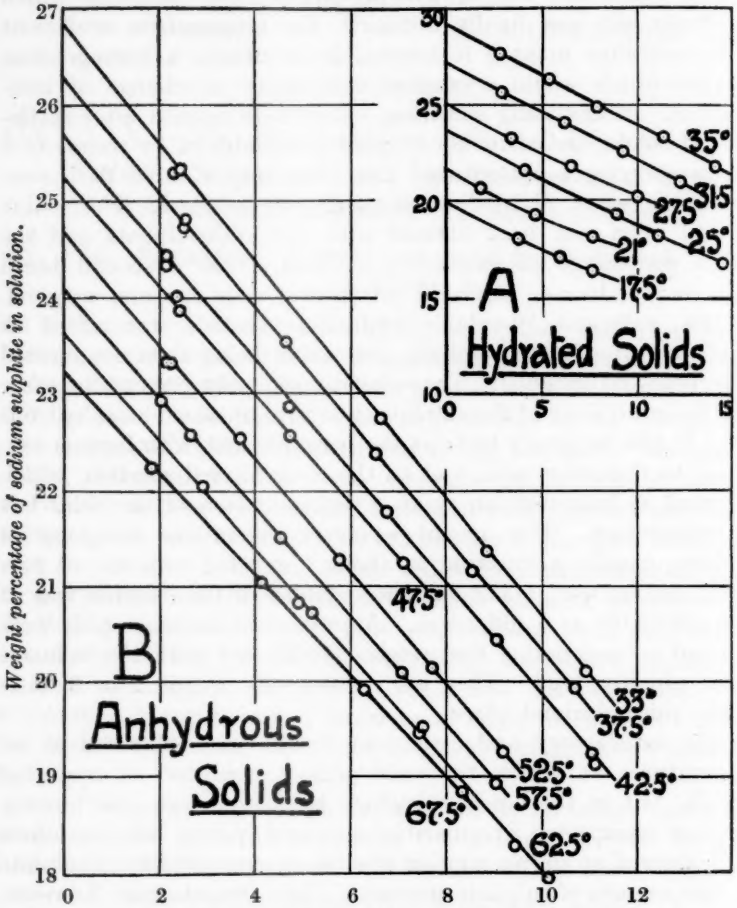


Table I gives the figures for those temperatures at which hydrated solids were stable and also for the metastable series at 35°, which was quite easily followed. Compositions are in percentages of respective salts by weight; the figures for water, obtainable by difference, are not quoted.

The results are plotted in Fig. 1*A* at the top right-hand corner.

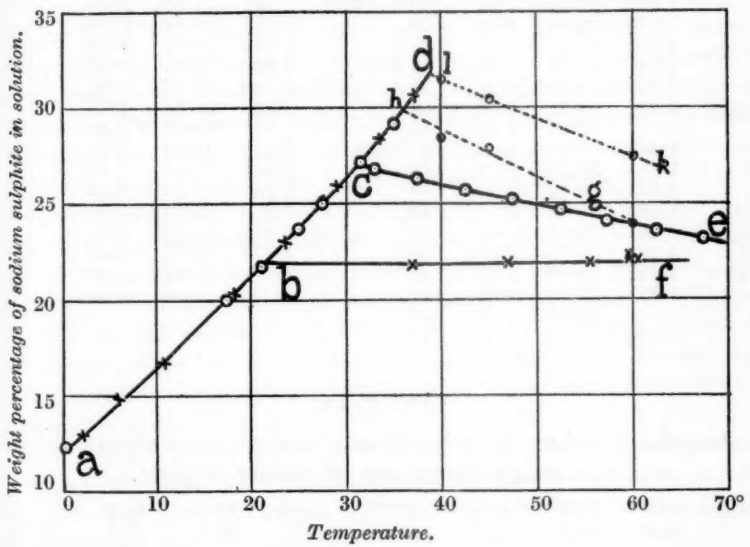
TABLE I.

Hydrated solids.

Temp.	$D_4^{t°}$.	Percentage composition of solution. Na_2SO_3.	Na_2SO_4.	Temp.	$D_4^{t°}$.	Percentage composition of solution. Na_2SO_3.	Na_2SO_4.
0·10°	1·125	11·59	1·11	27·5°	1·259	23·33	3·45
	1·129	11·34	1·76		1·273	21·87	6·52
	1·129	11·37	1·77		1·294	20·21	9·99
	1·129	11·37	1·79	31·5°	1·282	25·64	2·93
17·5°	1·215	18·04	3·79		1·300	24·09	6·08
	1·230	17·09	5·97		1·314	22·53	9·23
	1·239	16·45	7·59		1·332	21·00	12·22
	1·240	16·46	7·66	35·0°	—	27·69	2·83
	1·240	16·48	7·64		1·300	27·71	2·74
21·0°	1·218	20·64	1·84		1·312	26·41	5·16
	1·235	19·38	4·67		1·327	24·94	7·96
	1·252	18·09	7·62		1·338	23·39	11·30
25·0°	1·250	21·61	4·14		1·35	21·83	14·11
	1·274	19·44	8·97				
	—	18·27	11·05				
	1·312	16·81	14·54				
	1·312	16·77	14·50				

Extrapolation to zero sulphate is simple, and in Table II are the values so obtained for pure sodium sulphite heptahydrate.

FIG. 2.



These are shown by the circles in the curve *a b c d* of Fig. 2, whilst the crosses give the direct measurements of Hartley and Barrett (*loc. cit.*) with perfectly pure sulphite, recalculated to percentages by weight. It is readily seen that the agreement in

TABLE II.

Extrapolated values for solubilities of $Na_2SO_3,7H_2O$. a = weight percentage of sodium sulphite.

Temp.	0·10°	17·5°	21·0°	25·0°	27·5°	31·5°	35·0°
a	12·3	20·0	21·7	23·7	25·0	27·15	29·2

the two sets of results is quite good, and this gives confidence in the extrapolation method.

In Table III are the values for those temperatures at which anhydrous solids are stable.

TABLE III.

Anhydrous solids.

Temp.	$D_4^{t°}$.	Percentage composition of solution. Na_2SO_3.	Na_2SO_4.	Hours of rotation.	Temp.	$D_4^{t°}$.	Percentage composition of solution. Na_2SO_3.	Na_2SO_4.	Hours of rotation.
33·0°	—	25·29	2·30	14·5	52·5°	1·238	23·31	2·18	1·5
	1·269	25·33	2·44	35		—	23·31	2·24	22·5
	1·286	22·75	6·63	35		1·244	22·54	3·72	45
	1·295	21·36	8·87	35		1·254	21·29	5·80	45
	1·303	20·10	10·95	35		1·261	20·13	7·73	45
37·5°	1·260	24·73	2·51	45		1·267	19·26	9·20	45
	1·260	24·81	2·54	69	57·5°	1·230	22·93	2·03	11·5
	1·270	23·54	4·63	69		1·234	22·58	2·69	43
	1·280	22·38	6·52	83·5		1·243	21·50	4·56	43
	1·288	21·14	8·59	83·5		1·263	18·93	9·04	43
	1·297	19·94	10·70	83·5	62·5°	1·229	22·02	2·95	21
42·5°	1·251	24·32	2·17	22		1·238	20·82	4·91	21
	—	24·42	2·16	44		—	20·72	5·20	17·5
	1·263	22·88	4·72	44		1·250	19·52	7·52	17·5
	1·272	21·78	6·78	44		1·249	19·47	7·44	21
	1·283	20·42	9·06	22		1·257	18·28	9·48	21
	1·283	20·42	9·03	44		1·260	17·94	10·16	17·5
	1·291	19·11	11·15	22	67·5°	1·217	22·23	1·87	5
	1·290	19·23	11·07	44		1·227	21·01	4·16	5
47·5°	1·249	23·89	2·46	22		—	19·93	6·27	5
	1·250	24·03	2·40	42		1·248	18·85	8·35	5
	—	22·56	4·77	42					
	1·270	21·22	7·14	42					

TABLE IV.

Extrapolated values for solubilities of anhydrous sodium sulphite. a = weight percentage of sodium sulphite.

Temp.	33·0°	37·5°	42·5°	47·5°	52·5°	57·5°	62·5°	67·5°
a	26·8	26·3	25·7	25·25	24·7	24·1	23·6	23·2

Fig. 1*B* shows that these lie on curves that are straight lines within the limits of experimental error. The radius of each circle here represents about 1 part in 450 on the sulphite value. The extrapolated values for pure sulphite are quoted in Table IV and

plotted in the curve *c e* of Fig. 2: this intersects *a b c d* at about 31·5°, the corresponding concentration of sulphite being 27·2 per cent. The course of *c e* is downwards and rather like that of the curve giving the solubility of anhydrous sodium sulphate over much the same temperature range. Hartley and Barrett's curve, on the other hand, is horizontal, and is reproduced as *b f*. It intersects *a b c d* at *b*, the co-ordinates being 22° and 22 per cent. sulphite. In the last column of Table III are quoted the times for which tubes were rotated in thermostats. These varied considerably, and from the uniformity of the results it is evident that the equilibrium condition has always been reached. Hartley and Barrett gave similar fairly long times of contact (*loc. cit.*, p. 1183) in determining their saturation values.

It is a natural surmise that the marked discrepancy is due to the mixed crystals of sulphite and sulphate corresponding, in the limiting case of zero sulphate, with a form of sodium sulphite which is metastable to that obtained as a pure salt by Hartley and Barrett's method. For further information, a complete examination of the whole ternary system of sulphite, sulphate, and water was then carried out at temperatures where only anhydrous solids appeared, and the results of it, communicated in the next paper, show that these two salts are capable of mixing in quite a number of distinct series of crystals. In particular, at the sulphite end, two series were obtained by evaporation, under reduced pressure, of homogeneous unsaturated solutions, until solid appeared. Of these two series, one is metastable to the other, and apparently both are metastable to the curve for the solid present in B.D.H. anhydrous sulphite. The extrapolations from these are not very accurate, but are sufficiently so to show that there are two other transition points between anhydrous and hydrated sulphite. One of them, where the curve *g h* meets *a b c d*, in Fig. 2, is at approximately 30 per cent. of sulphite and 36°. The other, where *k l* meets *a b c d*, is in the neighbourhood of 31·5 per cent. and 39°. Mitscherlich's reported temperature of maximum solubility of sodium sulphite, 33°, is thus between *c* (31·5°) and *h* (36°). In all three curves, *k l*, *g h*, and *e c*, the extrapolated solubilities of sulphite diminish with increase of temperature, in contrast with Hartley and Barrett's curve, *b f*, where the temperature coefficient is practically zero.

These various possibilities of formation of mixed crystal series of sulphite and sulphate no doubt explain the irregular results obtained at first in those cases where anhydrous solid was formed in the complexes by heating hydrated crystals.

Summary.

1. By extrapolation to zero sulphate, of curves connecting saturation concentration of sodium sulphite in solutions containing up to 10 per cent. of sulphate, figures have been obtained which fully confirm Hartley and Barrett's results for the solubility of pure sodium sulphite heptahydrate.

2. Using commercial anhydrous sodium sulphite (already containing sulphate), a curve has been similarly obtained for the pure salt which indicates a transition point between it and the heptahydrate at 31·5° and 27·2 per cent. sulphite, whereas Hartley and Barrett, by direct measurements on pure salts, determined this point to be 22° and 22 per cent.

3. By evaporation of unsaturated solutions two other curves have been indicated, pointing to transition points of 36° and 30 per cent., and 39° and 31·5 per cent., respectively.

4. Evidently anhydrous sodium sulphite and sodium sulphate can form mixed crystals of varying stabilities, and the corresponding solids free from sulphate, if obtainable, would prove to be metastable relatively to the ordinary pure form of sulphite with a transition point at 22°.

UNIVERSITY OF MELBOURNE. [*Received, March 24th*, 1924.]

CXL. — *Miscibility of Anhydrous Sulphite and Sulphate of Sodium.*

By NEIL BANNATYNE LEWIS and ALBERT CHERBURY DAVID RIVETT.

THAT anhydrous sodium sulphite and sulphate could form mixed crystals in at least three, and possibly four, distinct series at 25° (metastable) and 37·5° was shown incidentally in a recent paper (*Rec. trav. chim.*, 1923, **42**, 954), which dealt mainly with the hydrated salts. These observations, together with those recorded in the preceding paper, pointed to the desirability of further investigation into the ternary system sulphite–sulphate–water at temperatures at which only anhydrous solid phases could exist.

For satisfactory results, it is necessary to form the solid at the temperature of experiment from homogeneous solutions. In a system such as this, this means that water must be evaporated from unsaturated solutions of suitably chosen concentrations. At temperatures from about 40° upwards, gentle boiling is readily brought about at pressures easily attained with a water-pump. The procedure adopted has been to rock in a thermostat tubes

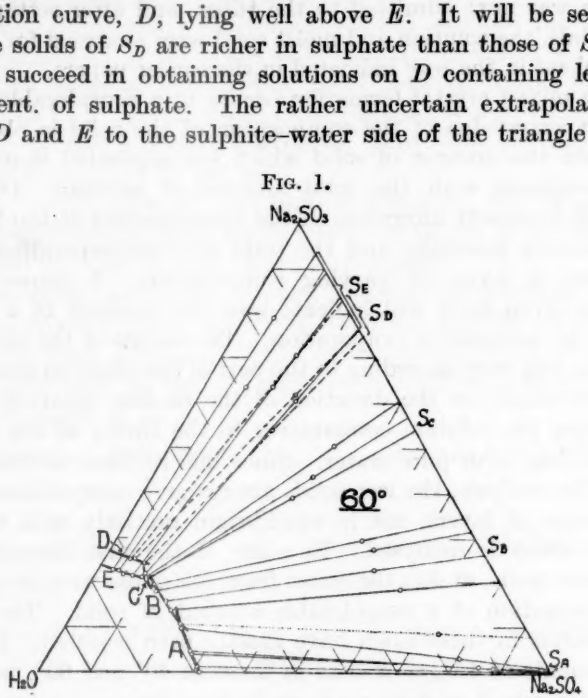
containing some 80 grams of unsaturated solution, the tubes carrying at right angles side pieces to which lengths of pressure tubing were attached. Usually six tubes were handled at once, their tubings being connected to a receiver exhausted to suitable pressure. After sufficient evaporation, crystals separated, although sometimes a considerable degree of supersaturation was first reached. Nitrogen was next admitted to the tubes, and after settlement of the crystals, the solution and moist solid were analysed for sulphite and sulphate in the way indicated in the earlier papers.

Where mixed crystal formation occurs to a considerable extent, a correct knowledge of the composition of the solid is obtainable only when the amount of solid which has separated is negligibly small compared with the total amount of solution. Otherwise there will be steady alteration in the concentration of the latter as crystallisation proceeds, and the solid may correspondingly be a succession of layers of varying compositions. A glance at the diagrams given later will indicate how the position of a solid is changed by progressive evaporation. The extent of the error from this cause will vary according to the part of the diagram considered, being dependent on the direction of the tie-line relatively to the line joining the solution composition to the corner of the triangle corresponding with pure water. Since one requires several grams of solid for analysis, the wet solids always give compositions which are averages of layers, not in equilibrium precisely with the final solution which is analysed. In some of the first measurements which were made, at 45°, the errors from this cause were large owing to the formation of a considerable amount of solid. The figures for the solids in these cases have mostly been rejected. In other measurements at 45°, as well as in those at 40° and 60°, we aimed at forming only 2 or 3 grams from at least 50 grams of saturated solution; but it was difficult always to judge the amount, especially when supersaturated solutions were produced. The precise limits of the series of mixed crystals found are therefore uncertain, but the error is not sufficient to affect the general conclusions. Altogether, more than eighty solutions have been examined and apart from certain moist solids at 45° and one or two other complexes at 60° all measurements which have been made are recorded in the sequel.

Table I gives the analyses at 60°, concentrations of salts being in percentages by weight. These are plotted in Fig. 1 and point to the conclusion that there are no fewer than five solution curves, lettered A to E, respectively, and five corresponding series of mixed crystals, lettered S_A to S_E. Of these, S_A is very short: sodium sulphite does not mix freely with sulphate when the solid

is formed in solutions relatively very rich in the latter. With solutions containing above about 10 per cent. of sulphite, a break occurs, and in the new series, S_B, the solid contains a higher percentage of sulphite than does the solution. The third series, S_C, is not very extensive at 60°; it is greater at 40°. Of the remaining series, S_D and S_E, the former is metastable relatively to the latter, its solution curve, D, lying well above E. It will be seen, too, that the solids of S_D are richer in sulphate than those of S_E. We did not succeed in obtaining solutions on D containing less than 5 per cent. of sulphate. The rather uncertain extrapolations of curves D and E to the sulphite–water side of the triangle (which,

FIG. 1.



with those at 40° and 45°, have been used in the preceding paper) give about 27·5 and 24 per cent. of salt, respectively. The latter figure is practically the same as that obtained by extrapolation from measurements (preceding paper) in which commercial anhydrous sodium sulphite was shaken in excess with solutions of varying concentration of sulphate. But although it extrapolates to the same point, the course of the latter curve is definitely below E. At 40°, the distance between them is greater throughout. Hartley and Barrett's measurements (J., 1909, **95**, 1178) would seem to indicate the possibility of yet a fourth curve in this region, although probably it is realisable only exceedingly close to the sulphite side. It appears, then, that the greater het metastability of the solid produced, the greater the concentration of sulphate in it and the greater the concentration of sulphite in its saturated solution.

TABLE I.

60°.

Percentage composition.					
	Solution.		Moist solid.		Solid Series.
$D^{t°}_{4°}$.	Na_2SO_3.	Na_2SO_4.	Na_2SO_3.	Na_2SO_4.	
1·295	1·01	30·26	0·30	89·0	S_A
1·300	3·90	27·84	1·17	85·3	
1·300	4·24	27·48	0·91	88·3	
1·311	9·76	22·69	3·04	80·6	
1·316	10·92	22·02	8·88	73·7	Trans. S_A and S_B.
1·309	13·60	18·59	18·30	61·1	S_B
1·309	15·56	16·59	22·73	53·9	
—	17·78	13·66	27·27	51·3	
1·308	19·37	12·52	29·34	48·03	
1·297	20·27	10·62	43·7	31·1	S_C
1·299	20·79	10·35	38·8	29·6	
1·298	20·87	10·13	50·2	31·9	
1·303	21·86	9·56	—	—	
1·311	24·17	8·05	53·8	18·01	S_D
1·297	25·09	5·70	61·7	18·53	
1·287	25·03	4·94	70·5	14·42	
1·290	20·99	9·25	60·4	19·17	S_E
1·271	21·37	7·20	63·6	13·15	
1·250	21·60	5·26	75·0	7·55	
1·249	22·47	3·96	—	—	
1·240	22·82	2·83	79·0	5·59	

TABLE II.

40°.

Percentage composition.					
	Solution.		Moist solid.		Solid series.
$D^{t°}_{4°}$.	Na_2SO_3.	Na_2SO_4.	Na_2SO_3.	Na_2SO_4.	
1·317	1·03	31·6	0·41	80·8	S_A
1·322	3·73	29·3	1·21	81·1	
1·326	6·43	26·8	2·14	78·1	
1·332	8·99	24·5	3·07	77·5	
1·340	12·83	21·5	4·15	76·4	
1·342	13·01	21·2	8·19	69·7	Trans. S_A and S_B
1·342	12·61	21·6	12·06	63·3	S_B metastable.
1·343	14·54	20·03	17·13	59·3	S_B
1·340	16·76	17·30	18·93	58·4	
1·339	17·85	16·09	20·02	58·5	
1·336	19·53	14·23	22·13	54·9	
1·334	20·74	12·71	24·19	52·4	
1·345	24·49	9·92	28·0	51·0	
1·342	25·38	8·41	30·6	48·7	
1·350	18·07	16·78	—	—	S_C
1·345	20·01	14·30	24·8	53·4	
1·339	22·33	11·49	29·7	47·5	
1·342	22·63	11·34	31·7	49·5	
1·336	22·76	10·80	30·1	43·4	
1·335	25·06	8·25	36·1	41·5	
1·349	27·46	7·09	45·4	22·3	?
1·349	27·60	7·02	48·4	25·3	
1·356	28·63	6·75	46·0	23·0	
1·334	25·58	7·73	—	—	S_D
1·322	26·08	5·88	58·8	20·07	
1·323	27·52	4·79	61·7	17·65	
1·314	23·62	8·07	—	—	S_E
1·306	23·80	6·90	—	—	
1·298	24·89	5·24	71·1	11·95	
1·288	26·47	2·67	74·0	9·49	
1·298	27·61	0·87	73·6	9·08	

TABLE III.

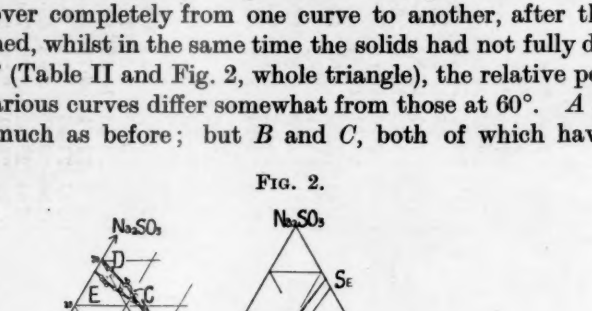
45°.

Percentage composition.					
	Solution.		Moist solid.		Solid series.
$D^{t°}_{4°}$.	Na_2SO_3.	Na_2SO_4.	Na_2SO_3.	Na_2SO_4.	
1·312	2·01	30·16	0·69	81·1	S_A
1·323	7·56	25·58	1·54	89·6	
1·324	7·51	25·57	1·80	88·5	
1·327	9·62	24·05	3·91	75·0	
1·331	12·93	20·66	—	—	S_B
1·333	15·05	18·68	18·73	60·0	
1·327	17·47	15·81	—	—	
1·334	19·85	13·87	22·49	50·5	
1·327	22·36	10·60	27·94	48·3	Unstable
1·320	20·52	12·01	—	—	S_C
1·315	22·33	9·92	42·5	38·6	
1·323	23·81	8·87	—	—	
1·321	24·72	7·84	41·82	36·3	
1·328	25·52	7·61	43·96	33·4	
1·320	24·10	8·59	50·9	22·1	Trans. S_C and S_D
1·315	24·75	7·28	—	—	S_D
1·296	26·35	3·86	64·9	12·32	
1·306	28·06	2·90	—	—	
1·298	28·19	2·29	66·7	9·31	
1·280	26·36	2·56	74·9	7·71	Unstable
1·310	21·33	10·43	67·6	11·2	S_E
1·298	22·71	7·78	—	—	
1·297	23·48	7·11	—	—	
1·290	23·91	5·88	69·7	10·07	
1·288	23·82	5·96	75·7	9·75	
1·275	24·61	3·79	74·1	7·99	
1·292	24·64	3·85	—	—	
1·275	25·16	3·11	—	—	
1·273	25·89	2·29	73·1	3·71	
1·273	26·53	1·79	—	—	

Not only are there these metastable systems in the left of the diagram, but metastable points on curves *B* and *C* (produced) are obtainable. This adds difficulty to the work, for a metastable system is liable to change when the tube is opened, or during analysis after the insertion of the pipette. Several of the solutions examined were obviously in process of change, whilst others had passed over completely from one curve to another, after the tube was opened, whilst in the same time the solids had not fully done so.

At 40° (Table II and Fig. 2, whole triangle), the relative positions of the various curves differ somewhat from those at 60°. *A* and S_A remain much as before; but *B* and *C*, both of which have been

FIG. 2.



continued into metastable regions, correspond with series of solids which overlap in composition. Hence any merging of these two curves at a critical solid solution temperature, such as has been observed in the system ammonium chloride–manganous chloride dihydrate (J., 1923, **123**, 1350), would seem impossible. *D* and *E* are steeper than at 60°, and the slopes of their respective tie-lines differ more from one another than they do at 60°, where, indeed, there is overlapping between S_D and S_E. Extrapolations of *D* and *E* to the binary system give 28·5 and 31·5 per cent. of sulphite, respectively.

The meaning of the points the tie-lines of which are marked with a query in Fig. 2 is ambiguous. They may correspond with yet another and still more unstable system, the solution curve of which lies above *D*, just as *D* does above *E*, and *E* above that

obtained (previous paper) with commercial sulphite, whilst the solid series lies below S_D just as this lies below S_E. On the other hand, these points may represent systems which crystallised on the metastable upward extension of curve B and were analysed during the change to less metastable states both of liquid and solid.

The figures obtained at 45° are given in Table III and the solutions are plotted in the small portion of a triangle included on the left of Fig. 2. Here again the existence of five distinct curves is confirmed. The extrapolations of D and E to the binary system are 28·0 and 30·5 per cent. of sodium sulphite, respectively.

UNIVERSITY OF MELBOURNE. [*Received, March 24th*, 1924.]

CXLI.—*The Influence of the Orientation of Surface Molecules on the Surface Tension of Pure Liquids.*

By SAMUEL SUGDEN.

THE properties of thin films on water have led many workers to the conclusion that the molecules in these films are arranged in definite positions with respect to the water surface. Certain groups of atoms, for example, the carboxyl group, are presumed to be attracted by water and anchored in the surface, while other parts of the molecule which are less strongly attracted constitute the outer edge of the film. Thus a film of palmitic acid is supposed to consist of a marshalled assembly of molecules with all the carbon chains normal to the water surface and the carboxyl groups on the surface of the water.

These conceptions have been used as a basis for the discussion of the surface tension of pure liquids by Langmuir (*Chem. and Met. Eng.*, 1916, **15**, 468; *J. Amer. Chem. Soc.*, 1917, **39**, 1848) and by Harkins, Davies, and Clark (*J. Amer. Chem. Soc.*, 1917, **39**, 541). The views put forward by these writers involve two hypotheses, namely:

(*a*) The molecules in the surface layer of a liquid are oriented, or arranged in definite directions in space so that the most strongly attracted groups are nearer the bulk of the liquid than those which are less strongly attracted.

(*b*) The total surface energy of the liquid is determined chiefly by the external groups of atoms and is little affected by the strongly attracted groups which are drawn into the body of the liquid.

Langmuir and Harkins, Davies, and Clark discuss a large amount of surface tension data from this point of view and in particular

draw definite conclusions about benzene and its substitution products. In benzene, it is supposed that the ring of carbon atoms lies parallel to the plane of the liquid surface. The introduction of another atom or group of atoms, as in chlorobenzene and nitrobenzene, produces an unsymmetrical molecule and the ring then stands normal to the liquid surface with the strongly attracted substituent within the liquid. Symmetrical *p*-disubstitution products, for example, *p*-dichlorobenzene, have about the same surface energy as benzene, whilst an unsymmetrical derivative of this type, for example, *p*-nitrochlorobenzene, has a much higher surface energy which is accounted for by assuming that the plane of the ring is perpendicular to the liquid surface with one of the substituent groups at its outer end.

It is easily seen that if molecules do arrange themselves in this fashion in the surface layers of a liquid there is little hope of discovering a relation between surface tension and chemical constitution which would be even approximately additive. The presence of a strongly attracted group in the molecule might be entirely masked, for it would produce no appreciable effect on the surface energy unless its introduction into the molecule happened to bring into the outer surface another group as in the case of *p*-nitrochlorobenzene. On the other hand, a study of the orientation of a series of molecules might, if the orientation hypothesis were correct, give some information as to the relative attracting power of different groupings, which, on Langmuir's view of the identity of chemical and cohesive forces, would be expected to bear a relation to the chemical reactivity of the groups concerned.

The quantity which is presumed to be determined largely by the exterior atoms or groups is the total surface energy or $\gamma - T d\gamma/dT$, where γ is the surface tension at an absolute temperature T. This expression gives the total surface energy per square cm. and an error is introduced in comparing these values if the molecules of the liquids examined do not all occupy the same area on the surface. To get over this difficulty, one may limit the discussion to *p*-disubstituted benzene derivatives, $X \cdot C_6H_4 \cdot Y$. If X and Y are dissimilar groups and the molecule is oriented with the XY axis normal to the liquid surface, then the area on the surface occupied by a molecule will be constant for all substances of this type and will correspond to the cross-section of the benzene ring system. Unit area of surface will therefore contain equal numbers of such oriented molecules and the total surface energy per sq. cm. may be used in seeking the regularities which are discussed below.

Assuming that hypotheses (*a*) and (*b*) are correct, it is easily seen that certain numerical relations should exist between the

total surface energies of *p*-substituted benzene derivatives. Consider a series of substances in which the group X is constant but in which the groups Y_1, Y_2, Y_3 are substituted for Y, the groups being arranged in the order of their residual affinity. As long as the group X is more strongly attracted than the group Y, the molecules will arrange themselves so that X is within the liquid. Hence by hypothesis (*b*) the total surface energy will increase in the order Y_1, Y_2, Y_3, as these external groups will determine the total surface energy. If we suppose that the residual affinity of X is greater than that of Y_3 but less than that of Y_4, Y_5, Y_6, then in compounds with the latter three groups in the para-position to X the groups Y_4, Y_5, Y_6 will be drawn into the liquid. All these compounds will have the group X outside and should all have the same total surface energy, which will be greater than that of the compounds containing the groups Y_1, Y_2, Y_3.

If now we consider a series of compounds in which Y_2 is the constant group, it will readily be seen that the total surface energy of any compound of this series can never be greater than that of the compound with the groups Y_2 and X, for in this compound the group Y_2 is already at the outer end of the molecule.

To test these conclusions, three series of compounds have been studied. Details of the purification of the substances used and of the methods of measurement are given in the experimental part of the paper. Before considering the results, it is necessary to discuss the question of the constant which must be chosen for the purpose of tracing the relations referred to above.

Langmuir chose the total surface energy, since he supposed that it was independent of temperature. It has recently been shown by the author (this vol., p. 32) that the variation of surface tension with temperature is represented with considerable accuracy by the equation

$$\gamma = \gamma_0 (1 - m)^{6/5} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

from which it follows that the total surface energy is given by the expression

$$\gamma - Td\gamma/dT = \gamma_0(1 + m/5)\ (1 - m)^{1/5} \quad . \quad . \quad . \quad . \quad (2)$$

In these equations, m is the reduced temperature. It will be seen that the total surface energy is not independent of temperature, but has the value γ_0 at absolute zero. As the temperature rises, this energy decreases, at first slowly and later more rapidly and becomes zero at the critical point. Hence the values of γ_0 are proportional to the total surface energy at corresponding temperatures. These values are collected in Table I, whilst Table II gives the total surface energy at the boiling point calculated by (2). Both tables

lead to the same conclusions; the second one is recorded because the boiling point has frequently been used as a comparison temperature. Since boiling points are not precisely corresponding temperatures, the relative magnitudes of the constants in the two tables differ to some extent.

TABLE I.

Values of γ_0.

	Y =	CH_3.	H.	Cl.	Br.	I.	NO_2.	NH_2.
X	H	65·33	70·26	71·01	74·48	77·07	81·70	82·40
	Cl	66·65	71·01	71·45	71·83	74·71	78·68	81·37
	CH_3	—	65·33	66·65	66·46	69·28	74·06	68·19

TABLE II.

Total surface energy at the boiling point.

	Y=	CH_3.	H.	Cl.	Br.	I.	NO_2.	NH_2.
X	H	59·77	64·78	64·71	68·60	70·53	74·50	75·85
	Cl	60·64	64·71	65·10	65·81	68·35	71·45	75·29
	CH_3	—	59·77	60·64	60·64	63·19	67·06	62·84

The first series of compounds consists of monosubstituted benzene derivatives and the constant group is the hydrogen atom. It will be seen from the tables that the total surface energies at absolute zero and at the boiling point increase steadily from toluene to aniline along the first row of the tables. From the argument advanced above, this indicates that none of the substituent groups is attracted so strongly as the hydrogen atom, which must be drawn within the liquid, whilst the different surface energies must be ascribed to the presence of different substituents at the outer end of the molecule. This conclusion is directly opposed to that drawn by Langmuir and Harkins (*loc. cit.*), who suppose that in chlorobenzene the chlorine atom is attracted strongly and causes the benzene ring to be arranged at right angles to the liquid surface.

Accepting, for the moment, the view that in the first series the substituent group is at the outer end of the molecule and determines the total surface energy, it follows that the value for toluene should be the maximum for the third series and that for chlorobenzene the maximum for the second series. Inspection shows that this is not true; in both series the total surface energy increases considerably when groups such as the NO_2 radical are introduced into the molecule.

The general conclusion to be drawn from this work is, therefore, that the total surface energy of a pure liquid is not determined by one part of the molecule only, but depends on the nature of the molecule as a whole. That is to say, hypothesis (*b*) is not substantiated. As regards the first hypothesis, it is not possible from observations of this kind to decide whether the molecules on the

surface do or do not possess a special orientation. Such an arrangement would seem improbable from the standpoint of the kinetic theory, and the supposed influence of the regular marshalling of molecules on the total surface energy is not verified by experiment.

The data obtained in this investigation have been used to test the relation discovered by Macleod (*Trans. Faraday Soc.*, 1923, **19**, 38). The last column of the tables in the experimental part of the present paper gives the value of $\gamma^{1/4}/(D - d)$. It will be seen that this quantity is independent of temperature except for the three amines. These compounds are usually regarded as associated liquids, and, like alcohol and acetic acid, give a value for the Macleod constant which increases slowly with increasing temperature.

Experimental.

The determinations of surface tension were carried out by method of maximum bubble pressure (J., 1922, **121**, 860; this vol., p. 27). Six bubblers were employed, each substance being measured on two instruments. The constants for the tubes used are given below.

Apparatus	III.	1.	3.	3*a*.	4.	5.
r_2 cm. ...	0·159	0·163	0·159	0·159	0·139	0·140
A	0·005271	0·003736	0·003333	0·006080	0·004641	0·006462

The densities are derived largely from the work of Perkin (J., 1896, **69**, 1025), Young (*Proc. Roy. Dublin Soc.*, 1909–1910, **12**, 374), Bramley (J., 1916, **109**, 10, 304), and Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1). In some cases new determinations have been made with a U-shaped dilatometer having a wide limb and a graduated capillary limb with a bulb at the base. The substance, if solid at the ordinary temperature, was placed in the wide limb, melted, and then drawn into the bulb to determine its volume. The instrument used was calibrated by means of mercury; the bulb had a capacity of about 3 c.c. and one scale division of the capillary limb was equal to 0·000513 of the bulb volume. It is estimated that the densities determined in this manner are accurate to 1 part in 2000 parts.

In the tables given below, the first column indicates the apparatus used, and the second the temperature of observation. The thermometer used was standardised at the National Physical Laboratory, and a correction applied for exposed stem. P is the difference in the pressures required to liberate bubbles from the two tubes expressed in dynes/cm.^{2}, D and d are the densities of liquid and vapour, respectively, in gram/c.c., and ϕ is the correction factor calculated by the equation.

$$\phi = 1 + 0{\cdot}69r_2gD/P \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here $g = 981$ cm./sec.^{2} and r_2 is the radius of the wider tube in cm. The surface tensions in the sixth column are expressed in dynes/cm.; the figures in the seventh column are calculated by the formula given immediately below the table, and the eighth column gives the difference between the observed and calculated figures. The figures in the last column should be constant if Macleod's relation is true (*loc. cit.*). It will be seen that the values are sensibly constant except for the three amines.

Benzene and Chlorobenzene.—The data for these substances have already been given (this vol., p. 37).

Bromobenzene.—A commercial sample was fractionally distilled three times, and then boiled at 155° (corr.)/749 mm. The densities are due to Young (*loc. cit.*).

App.	t.	P dyn./cm.^{2}.	$D-d$ gm./c.c.	ϕ.	γ (obs.) dyn./cm.	γ (calc.).	Diff.	$\gamma^{1/4}/(D-d)$.
1	15°	9982	1·501	1·017	37·92	37·96	+0·04	1·653
3	42	10,315	1·465	1·015	34·92	34·75	−0·17	1·659
1	49	8885	1·456	1·018	33·78	33·89	+0·11	1·656
3	78	9068	1·417	1·017	30·73	30·58	−0·15	1·662
1	90	7690	1·401	1·020	29·30	29·20	−0·10	1·661
1	105	7243	1·378	1·021	27·62	27·50	−0·12	1·663
1	125	6625	1·349	1·022	25·30	25·25	−0·05	1·663
1	139	6215	1·328	1·024	23·77	23·70	−0·07	1·663
3	150	6613	1·311	1·021	22·50	22·49	−0·01	1·661

$$\gamma = 74{\cdot}48\ (1 - \theta/670)^{6/5}.$$

Iodobenzene.—This was prepared from redistilled aniline, washed with alkali and acid, dried, and fractionated. The specimen used boiled at 186° (corr.)/752 mm. and was colourless when freshly prepared, but slowly developed a yellow colour. The densities are due to Young (*loc. cit.*).

App.	t.	P.	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\gamma^{1/4}/(D-d)$.
III	14°	7620	1·840	1·026	41·21	41·30	+0·09	1·377
3	50	10,885	1·785	1·018	36·93	37·11	+0·18	1·381
III	98	5823	1·711	1·031	31·63	31·62	−0·01	1·386
III	124	5286	1·670	1·034	28·80	28·72	−0·08	1·387
III	146	4808	1·634	1·037	26·27	26·30	+0·03	1·385
III	169	4367	1·595	1·039	23·91	23·81	−0·10	1·386
3	180	6592	1·575	1·026	22·64	22·63	−0·01	1·385

$$\gamma = 77{\cdot}07\ (1 - \theta/708)^{6/5}.$$

Nitrobenzene.—A commercial specimen was frozen six times and fractionally distilled. The specimen used boiled at 209° (corr.)/747 mm. The densities below 100° are due to Perkin and Jaeger (*loc. cit.*). New determinations for higher temperatures were made with the apparatus described above.

Densities determined: $D_4^{88°}$ 1·137, $D_4^{116°}$ 1·110, $D_4^{135°}$ 1·091, $D_4^{157°}$ 1·072, $D_4^{180°}$ 1·047.

App.	t.	P.	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\frac{\gamma^{1/4}}{D-d}$.
3	12°	13,440	1·210	1·011	45·29	45·15	−0·14	2·144
3	57	11,747	1·167	1·012	39·63	39·74	+0·09	2·150
III	90	6659	1·135	1·018	35·72	35·85	+0·13	2·154
3	100	10,277	1·125	1·013	34·69	34·61	−0·08	2·142
III	135	5670	1·092	1·021	30·52	30·66	+0·14	2·153
3	153	8450	1·074	1·014	28·57	28·62	+0·05	2·153
III	167	5015	1·060	1·022	27·00	27·05	+0·05	2·150
3	197	7048	1·029	1·017	23·89	23·74	−0·15	2·150

$$\gamma = 81{\cdot}70\ (1 - \theta/731)^{6/5}.$$

Aniline.—Aniline A.R. was fractionally distilled twice. The specimen used boiled at 183° (corr.)/752 mm. The densities are due to Bramley (*loc. cit.*).

App.	t.	P.	$D-d$.	ϕ.	γ (obs.).	γ(calc.).	Diff.	$\frac{\gamma^{1/4}}{D-d}$.
1	15°	11,765	1·0261	1·010	44·39	44·49	+0·10	2·516
3	39	12,335	1·0054	1·010	41·53	41·53	±0·00	2·525
1	66	10,150	0·9821	1·011	38·33	38·22	−0·11	2·534
3	104	9965	0·9483	1·012	33·62	33·66	+0·04	2·540
3	164	7860	0·8905	1·014	26·57	26·67	+0·10	2·550

$$\gamma = 82{\cdot}40\ (1 - \theta/717)^{6/5}.$$

p-*Dichlorobenzene.*—A commercial specimen was crystallised twice from absolute alcohol, and then melted sharply at 54° (corr.). The densities are due to Jaeger (*loc. cit.*).

App.	t.	P.	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\frac{\gamma^{1/4}}{D-d}$.
III	68°	5692	1·234	1·023	30·69	30·72	+0·03	1·908
III	96	5116	1·205	1·025	27·58	27·65	+0·07	1·902
III	117	4700	1·178	1·027	25·44	25·39	−0·05	1·906
3*a*	139	3646	1·154	1·034	22·92	23·06	+0·14	1·899
III	150	4062	1·142	1·030	22·05	21·84	−0·21	1·901
3*a*	166	3240	1·124	1·038	20·44	20·24	−0·20	1·898
III	170	3642	1·119	1·033	19·82	19·84	+0·02	1·893

$$\gamma = 71{\cdot}45\ (1 - \theta/675)^{6/5}.$$

p-*Chlorobromobenzene.*—This, prepared from *p*-chloroaniline and recrystallised from absolute alcohol, was obtained in white crystals melting sharply at 65° (corr.).

Densities determined: $D_4^{71°}$ 1·576, $D_4^{96°}$ 1·540, $D_4^{117°}$ 1·508, $D_4^{138°}$ 1·476, $D_4^{155°}$ 1·454.

App.	t.	P.	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\frac{\gamma^{1/4}}{D-d}$.
III	70°	6114	1·578	1·028	33·12	33·15	+0·03	1·520
4	102	6283	1·530	1·022	29·80	29·81	+0·01	1·528
III	106	5391	1·524	1·030	29·27	29·41	+0·14	1·527
III	132	4913	1·487	1·033	26·75	26·75	±0·00	1·529
4	164	4978	1·439	1·026	23·70	23·54	−0·16	1·534
4	194	4311	1·391	1·029	20·58	20·60	+0·02	1·531

$$\gamma = 71{\cdot}83\ (1 - \theta/722)^{6/5}.$$

p-*Chloroiodobenzene.*—This, prepared from *p*-chloroaniline and recrystallised from absolute alcohol, melted sharply at 54° (corr.).

Densities determined: $D_4^{57°}$ 1·886, $D_4^{81°}$ 1·849, $D_4^{99°}$ 1·831, $D_4^{111°}$ 1·797, $D_4^{137°}$ 1·756, $D_4^{151°}$ 1·736.

App.	*t.*	*P.*	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\frac{\gamma^{1/4}}{D-d}$.
4	61°	7913	1·879	1·021	37·53	37·57	+0·04	1·318
III	88	6445	1·835	1·031	35·02	34·78	−0·24	1·326
4	113	6761	1·795	1·024	32·16	32·22	+0·06	1·327
III	127	5684	1·773	1·033	30·93	30·80	−0·13	1·330
III	167	4892	1·707	1·038	26·76	26·82	+0·06	1·333

$\gamma = 74{\cdot}71\ (1 - \theta/767)^{6/5}$.

p-*Nitrochlorobenzene*.—The commercial product was crystallised three times from absolute alcohol and was obtained in almost colourless crystals melting sharply at 83° (corr.). The densities are due to Jaeger (*loc. cit.*).

App.	*t.*	*P.*	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\frac{\gamma^{1/4}}{D-d}$.
III	97°	6610	1·287	1·021	35·57	35·73	+0·16	1·897
III	111	6346	1·271	1·022	34·18	34·23	+0·05	1·902
4	127	6895	1·255	1·016	32·50	32·52	+0·02	1·903
III	141	5761	1·239	1·024	31·10	31·05	−0·05	1·906
III	156	5457	1·222	1·025	29·49	29·48	−0·01	1·907
4	179	5726	1·197	1·019	27·07	27·19	+0·12	1·905
III	186	4862	1·188	1·027	26·31	26·38	+0·07	1·906

$\gamma = 78{\cdot}68\ (1 - \theta/768)^{6/5}$.

p-*Chloroaniline*.—This was prepared by reduction of *p*-nitrochlorobenzene and purified by steam distillation and repeated crystallisation from absolute alcohol. It was obtained as white crystals melting sharply at 70° (corr.).

Densities determined: $D_4^{77°}$ 1·169, $D_4^{105°}$ 1·140, $D_4^{118°}$ 1·127, $D_4^{132°}$ 1·112, $D_4^{159°}$ 1·086.

App.	*t.*	*P.*	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\frac{\gamma^{1/4}}{D-d}$.
3*a*	81°	6437	1·164	1·016	39·75	39·72	−0·03	2·157
3*a*	117	5776	1·126	1·021	35·86	35·79	−0·07	2·173
4	133	7296	1·108	1·013	34·20	34·06	−0·14	2·183
3*a*	153	5107	1·088	1·023	31·76	31·93	+0·17	2·182
4	185	6070	1·053	1·015	28·59	28·57	−0·02	2·196

$\gamma = 81{\cdot}37\ (1 - \theta/787)^{6/5}$.

Toluene.—The data recorded below are due to Walden and Swinne (*Z. physikal. Chem.*, 1912, **79**, 700). The surface tensions are corrected as indicated by the author in a previous communication (this vol., p. 32).

t.	γ(W. & S.).	γ(corr.).	γ(calc.).	Diff.	$D-d$.	$\frac{\gamma^{1/4}}{D-d}$.
21·2°	27·39	28·30	28·30	±0·00	0·8626	2·674
27·1	26·73	27·62	27·62	±0·00	0·8569	2·675
65·3	22·46	23·21	23·25	+0·04	0·8198	2·677
77·8	21·11	21·81	21·80	−0·01	0·8073	2·677
92·5	19·57	20·22	20·22	±0·00	0·7921	2·678
104·0	18·36	18·97	18·96	−0·01	0·7798	2·677

$\gamma = 65{\cdot}33\ (1 - \theta/586)^{6/5}$.

p-*Chlorotoluene.*—The commercial product was fractionated twice and the specimen used boiled at 163·5° (corr.)/764 mm. The densities are due to Perkin and Jaeger (*loc. cit.*).

App.	*t.*	*P.*	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\frac{\gamma^{1/4}.}{D-d}$
4	25°	6846	1·065	1·015	32·24	32·08	−0·16	2·237
5	50	4426	1·039	1·022	29·22	29·38	+0·16	2·238
4	64	5930	1·025	1·016	27·96	27·90	−0·06	2·244
5	79	3955	1·010	1·024	26·17	26·31	+0·14	2·240
4	108	4936	0·979	1·019	23·32	23·30	−0·02	2·245
5	120	3331	0·966	1·028	22·11	22·08	−0·03	2·245
4	151	4030	0·933	1·022	19·11	18·95	−0·16	2·241

$$\gamma = 66{\cdot}65\ (1 - \theta/653)^{6/5}.$$

p-*Bromotoluene.*—This was prepared from *p*-toluidine. It was twice steam distilled and finally crystallised from absolute alcohol. The specimen used melted sharply at 27° (corr.). The densities are due to Perkin (*loc. cit.*).

App.	*t.*	*P.*	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\frac{\gamma^{1/4}.}{D-d}$
4	43°	6813	1·378	1·019	32·20	32·06	−0·14	1·729
5	60	4595	1·356	1·029	30·54	30·34	−0·20	1·734
4	81	5957	1·329	1·021	28·22	28·23	+0·01	1·735
5	100	3952	1·303	1·032	26·34	26·34	±0·00	1·739
4	122	5075	1·275	1·024	24·12	24·19	+0·07	1·738
5	131	3464	1·265	1·036	23·19	23·32	+0·13	1·735
4	164	4263	1·218	1·027	20·31	20·18	−0·13	1·743

$$\gamma = 66{\cdot}46\ (1 - \theta/694)^{6/5}.$$

p-*Iodotoluene.*—This was prepared from *p*-toluidine and recrystallised from absolute alcohol. The specimen used melted sharply at 34° (corr.).

Densities determined: $D_{4°}^{40}$ 1·678, $D_{4°}^{71°}$ 1·635, $D_{4°}^{102°}$ 1·591, $D_{4°}^{132}$ 1·547, $D_{4°}^{164°}$ 1·507.

App.	*t.*	*P.*	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\frac{\gamma^{1/4}.}{D-d}$
5	39°	5362	1·678	1·030	35·69	35·66	−0·03	1·456
4	59	8795	1·651	1·018	33·75	33·64	−0·11	1 460
5	78	4747	1·624	1·032	31·64	31·73	+0·09	1·461
4	100	7692	1·594	1·020	29·59	29·56	−0·03	1·460
5	122	4057	1·561	1·037	27·18	27·35	+0·17	1·459
4	140	6690	1·538	1·022	25·78	25·68	−0·10	1·463
5	166	3415	1·500	1·042	23·00	23·20	+0·20	1·466

$$\gamma = 69{\cdot}28\ (1 - \theta/734)^{6/5}.$$

p-*Nitrotoluene.*—The commercial product was recrystallised several times from absolute alcohol. The specimen used melted sharply at 51·8° (corr.). The densities are due to Jaeger (*loc. cit.*).

App.	t.	P.	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\gamma^{1/4}$. $D-d$.
5	56°	5686	1·122	1·019	37·41	37·23	−0·18	2·204
4	77	7401	1·103	1·014	34·82	35·02	+0·20	2·203
5	95	5023	1·086	1·021	33·14	33·15	+0·01	2·209
4	122	6409	1·061	1·016	30·22	30·39	+0·17	2·210
5	138	4355	1·047	1·024	28·81	28·78	−0·13	2·213
4	155	5712	1·031	1·017	26·95	27·07	+0·12	2·210
5	179	3757	1·008	1·026	24·90	24·70	−0·20	2·216
5	220	3142	0·968	1·030	20·91	20·68	−0·23	2·209

$$\gamma = 74{\cdot}06\ (1 - \theta/754)^{6/5}.$$

p-*Toluidine*.—The commercial product was steam distilled and recrystallised from ligroin. The specimen used was dried for several days over phosphoric oxide and melted at 44·5° (corr.). The densities are due to Bramley (*loc. cit.*).

App.	t.	P.	$D-d$.	ϕ.	γ(obs.).	γ(calc.).	Diff.	$\gamma^{1/4}$. $D-d$
4	51°	7295	0·961	1·012	34·26	34·32	+0·06	2·517
5	71	4943	0·943	1·019	32·52	32·38	−0·14	2·532
4	93	6436	0·925	1·014	30·29	30·26	−0·03	2·537
5	115	4292	0·907	1·021	28·30	28·15	−0·15	2·543
4	137	5520	0·889	1·015	26·00	26·08	+0·08	2·540
5	156	3676	0·869	1·023	24·29	24·31	+0·02	2·559
4	184	4598	0·838	1·017	21·70	21·74	+0·04	2·576

$$\gamma = 68{\cdot}19\ (1 - \theta/744)^{6/5}.$$

In some cases, for example, benzene, chloro- and bromo-benzene, nitrobenzene, and aniline, there is fair agreement between the surface tensions determined by Jaeger (*loc. cit.*) and by the author, but in others considerable discrepancies are found. Thus Jaeger's values for *p*-nitrochlorobenzene are 1—2 dynes/cm. lower than those given above, and similar differences occur in the data for iodobenzene, *p*-dichlorobenzene, *p*-chloroaniline, *p*-chlorotoluene, and *p*-bromotoluene. It is not easy to suggest an explanation of these differences, as Jaeger also employed the method of maximum bubble pressure. The figures given in the present paper were checked by making two series of measurements for each substance with different bubblers; the pressure gauge used was of simple type and could easily be kept clean. Jaeger used a gauge in which the movement of a mercury–octane interface through a few mm. displaced octane in a narrow tube, the movement of the mercury being deduced from observations of the octane meniscus. If the mercury–octane meniscus did not move as a whole but changed its shape to accommodate itself to small differences of pressure, this might account for the different values found by Jaeger and by the author.

Summary.

(1) The surface tension of fourteen derivatives of benzene has been measured over a considerable range of temperature.

(2) New determinations have been made of the densities in the liquid state of nitrobenzene, *p*-chlorobromobenzene, *p*-chloroiodobenzene, *p*-chloroaniline, and *p*-iodotoluene.

(3) It is shown from the data thus obtained that the Langmuir-Harkins hypothesis of the orientation of molecules on a liquid surface leads to the prediction of regularities in the total surface energy of benzene derivatives which is not verified by experiment. Hence it is concluded that even if the surface molecules of a liquid do possess a definite orientation, the total surface energy is not simply determined by those groups which are directed outwards, but by the molecule as a whole.

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CXLII.—*A Relation between Surface Tension, Density, and Chemical Composition.*

By SAMUEL SUGDEN.

THE relation between surface tension and density discovered by Macleod (*Trans. Faraday Soc.*, 1923, **19**, 38) appears to hold over a wide range of temperature (compare this vol., p. 32) and for substances of very different chemical properties (compare this vol., p. 1167). It therefore seems of interest to inquire whether this relation cannot be used to correlate the physical properties of density and surface tension with chemical composition. Macleod's relation is

$$\gamma = C(D - d)^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where γ is the surface tension and D and d the density of liquid and vapour all at one temperature. For non-associated substances, C is a characteristic constant independent of temperature.

If the fourth root of Macleod's constant is multiplied by the molecular weight the following expression is obtained.

$$P = \frac{M}{D - d}\gamma^{1/4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The quantity $M/(D - d)$ has the dimensions of volume and at low temperatures, where d becomes very small, is, in fact, the molecular volume. Hence a comparison of P for different substances is a

comparison of molecular volumes at temperatures at which the liquids have the same surface tension. The significance of this comparison will be seen when the magnitude of the internal pressure in a liquid is considered. This pressure (which for water at the ordinary temperature is of the order 11,000 atmospheres) is produced by the forces of attraction between the molecules which give rise to the phenomenon of surface tension and as a first approximation we may take the value of the surface tension as a measure of it. Macleod's rule gives us the relation between these two properties as the temperature varies and, as shown above, allows the molecular volumes to be compared at equal surface tensions, a procedure which for a property of the liquid seems more likely to lead to the discovery of regularities than the more commonly used method of comparison at the same vapour pressure (that is, at the boiling point).

If P is a true measure of the molecular volume, it should bear an approximately constant ratio to the critical volume; the table shows that the expression $P = 0{\cdot}78V_c$ can be used to predict the critical volume within about 3 per cent.

Substance.	P.	V_c	P/V_c.
Hydrogen	35·1	46·9	0·75
Benzene	206·3	256·1	0·81
Chlorobenzene	244·5	307·8	0·80
Diethyl ether	211·7	281·9	0·75
Carbon tetrachloride ...	219·9	276·1	0·80
Methyl formate	138·6	172·0	0·81
Ethyl acetate	217·1	286·0	0·76
			Mean 0·78

It will now be shown that the quantity P can be regarded as a function of chemical composition. For saturated substances, P is an additive function and for position isomerides has a nearly constant value. Unsaturation produces a marked effect, as does also ring formation, so that it seems probable that a comparison of values of P for a series of compounds will be of value in elucidating problems of chemical constitution. It is proposed to name this quantity the *parachor* (from $\pi\alpha\rho\alpha$ = by the side of, and $\chi\omega\rho\sigma\varsigma$ = space) to signify comparative volume.

The atomic constants for carbon and hydrogen can be deduced from molecular parachors in a rational manner. The difference for CH_2 in paraffins, esters, ethers, and ketones has a mean value of 39·0 and, by subtracting $n$$CH_2$ from a series of values for the paraffins C_nH_{2n+2}, sensibly constant values for 2H are obtained. The most probable values for carbon and hydrogen are C = 4·8 and H = 17·1.

If the data for the molecular volumes at the boiling point of the

lower paraffins are treated in this manner it is found that H = 0 and C = 22, but the figures do not form a very regular series and irregular differences of several units per cent. are found when these values are used to predict the observed figures. It is probably because the value 0 for hydrogen seems so improbable that special assumptions have always been made in discussing molecular volumes at the boiling point. Thus Kopp (*Annalen*, 1855, **96**, 153, 303) deduced his values for carbon and hydrogen from the relations $C_4H_{10} = C_6H_6 = 96$ and $CH_2 = 22$, thus neglecting constitutional influences, whilst Le Bas (" The Molecular Volumes of Liquid Chemical Compounds," Chap. 2, Longmans, Green and Co., 1915) supports his constants C = 14·7 and H = 3·7 by a comparison of a series of paraffins and olefines which neglects the influence of unsaturation.

In the tables which follow, a survey is made of the values of the parachor for 167 compounds for which data on surface tension and density are available. It has been found that the observed figures for this constant can be reproduced by adding together two sets of constants, one for the atoms in the molecule, the other for the constitutional influences of unsaturation and ring closure. The values for a particular atom appear to be independent of the manner in which it is situated in the compound and, with a few exceptions, position isomerism seems to cause no change in the parachor. This is true also for the constitutional factors, which are approximately constant from compound to compound. Thus a double bond between carbon and carbon has the same value as one between carbon and oxygen in the carbonyl group or between nitrogen and oxygen in the nitrosyl group. The same six-membered ring constant can be used for benzene, for *cyclo*hexane derivatives, and for pyridine, piperidine, and quinoline, while the same triple bond constant can be used for nitriles and the acetylenes. There is one important exception to this rule, namely the two oxygen atoms in the carboxyl group, which is discussed under the heading " Esters."

It appears probable that this simple addition of atomic and constitutional factors will require some modification when more precise values for the parachor are available. The tables which follow show, however, that this method of treatment gives a satisfactory basis for a preliminary classification of organic substances with respect to this constant.

The first table gives the values found for the most important atomic and structural parachors. Certain figures which are deduced from one or two compounds only, or which are based on somewhat doubtful data, are enclosed in brackets and can only be regarded as provisional values.

Atomic and structural parachors.

C	= 4·8	Triple bond	=(46·6)
H	= 17·1	Double bond	= 23·2
O	= 20·0	3-Membered ring	=(22·5)
N	=(12·5)	4-Membered ring	=(12·0)
F	=(25·7)	5-Membered ring	= 8·5
Cl	= 54·3	6-Membered ring	= 6·1
Br	= 68·0		
I	= 91·0	O_2 in esters	= 60·0

The figure for a four-membered ring was obtained from the observations of Mitchell and Smith on pinene and limonene (J., 1913, **103**, 489). Unfortunately, the varying densities found for different specimens of these substances show that the specimens examined were not pure. The figure quoted above was calculated from the difference between the parachors for the purest specimens of limonene and pinene as indicated by their densities and specific rotations. It is hoped shortly to obtain a direct value for this constant by measurements on pure *cyclo*butane derivatives.

In the tables which follow, the observers are indicated by initials, the full reference being given in the bibliography at the end of this paper.

Hydrocarbons.

No.	Substance.	Formula.	Observer.	*P* obs.	*P* calc.	% Diff.
1	Acetylene.	C_2H_2	M. & W.	88·6	90·4	+2·0
2	Ethylene.	C_2H_4	,,	99·5	101·2	+1·7
3	Ethane.	C_2H_6	,,	110·5	112·2	+1·6
4	Allylene.	C_3H_4	,,	122·9	129·4	+5·3
5	Propylene.	C_3H_6	,,	139·9	140·2	+0·2
6	Propane.	C_3H_8	,,	150·8	151·2	+0·3
7	Amylene.	C_5H_{10}	Sch.	218·2	218·2	±0·0
8	Benzene.	C_6H_6	R. & S.	206·3	207·1	+0·4
	,,	,,	Sch.	206·1	,,	+0·5
9	Diallyl.	C_6H_{10}	,,	248·2	246·2	−0·8
10	Methyl*cyclo*pentane.	C_6H_{12}	K.	242·8	242·5	−0·1
11	*n*-Hexane.	C_6H_{14}	Sch.	270·1	268·2	−0·4
	,,	,,	M. & C.	273·3	,,	−1·8
12	Toluene.	C_7H_8	W. & S.	246·9	246·1	−0·3
	,,	,,	Sch.	245·5	,,	+0·2
	,,	,,	M. & D.	246·5	,,	−0·2
	,,	,,	R. & Ca.	246·0	,,	+0·1
13	Methyl*cyclo*hexane.	C_7H_{14}	K.	278·5	279·1	+0·2
14	*n*-Heptane.	C_7H_{16}	K. & K.	309·3	307·2	−0·7
15	*o*-Xylene.	C_7H_{10}	Sch.	283·3	285·1	+0·7
	,,	,,	M. & D.	283·3	,,	+0·7
16	*m*-Xylene.	,,	W. & S.	284·6	,,	+0·2
	,,	,,	Sch.	283·8	,,	+0·5
	,,	,,	R. & G.	285·1	,,	±0·0
	,,	,,	M. & D.	284·3	,,	+0·3
17	*p*-Xylene.	,,	Sch.	283·8	,,	+0·5
	,,	,,	M. & D.	283·8	,,	+0·5
18	Ethylbenzene.	,,	Sch.	283·0	,,	+0·7
	,,	,,	M. & D.	283·8	,,	+0·5
19	1 : 1-Dimethyl*cyclo*hexane.	C_8H_{16}	K.	316·1	318·1	+0·7
20	Octine.	C_8H_{14}	W. & S.	327·4	324·4	−0·9

Hydrocarbons (*continued*).

No.	Substance.	Formula.	Observer.	*P* obs.	*P* calc.	% Diff.
21	Di*iso*butyl.	C_8H_{18}	Sch.	345·0	346·2	+0·4
22	*n*-Propylbenzene.	C_9H_{12}	,,	322·0	324·1	+0·7
23	*p*-Ethyltoluene.	,,	,,	321·7	,,	+0·8
24	Mesitylene.	,,	,,	320·5	,,	+1·1
	,,	,,	M. & D.	320·8	,,	+1·0
25	Cymene.	$C_{10}H_{14}$	Sch.	356·9	363·1	+1·7
	,,	,,	M. & D.	360·7	,,	+0·7
26	Di*iso*amyl.	$C_{10}H_{22}$	Sch.	422·7	424·2	+0·4
	,,	,,	M. & O.	425·7	,,	−0·4
	,,	,,	H. C. & R.	427·8	,,	−0·9
27	Undecine.	$C_{11}H_{20}$	W. & S.	404·5	441·4	+9·2
28	Diphenylmethane.	$C_{13}H_{12}$	M. & D.	419·0	419·0	±0·0
	,,	,,	H. & E.	414·5	,,	+1·1
29	$\alpha\alpha$-Diphenylethane.	$C_{14}H_{14}$	,,	449·8	458·0	+1·8
30	Diphenylpropane.	$C_{15}H_{16}$	,,	484·6	497·0	+2·5
31	Ditolylmethane.	,,	,,	488·0	,,	+1·8

The chief deviations are found with compounds containing a triple bond. Walden and Swinne's data for undecine (27) and for esters of phenylpropiolic acid (112) and (116) show very large deviations and it seems probable that the high densities found for these substances are due to incomplete purification. On the other hand, acetylene and octine (20) give a value for the triple bond which agrees well with that found from the data for nitriles. New measurements are now in progress on esters of phenylpropiolic acid and similar compounds which it is hoped will decide the value of the parachor for this linking.

Benzene and its derivatives are assumed to have the Kekulé formula and it will be seen that the predicted parachors are in good agreement with the observed figures.

Halogen Derivatives.

No.	Substance.	Formula.	Observer.	*P* obs.	*P* calc.	% Diff.
32	Carbon tetrachloride.	CCl_4	R. & S.	219·9	222·0	+1·0
	,, ,,	,,	Sch.	220·0	,,	+0·9
	,, ,,	,,	M. & T.	218·5	,,	+1·6
	,, ,,	,,	H. C. & R.	219·8	,,	+1·0
33	Chloroform.	$CHCl_3$	R. & C.	183·4	184·8	+0·8
	,,	,,	Sch.	183·4	,,	+0·8
	,,	,,	M. & T.	182·4	,,	+1·3
	,,	,,	H. C. & R.	183·5	,,	+0·7
34	Methylene dichloride.	CH_2Cl_2	,,	143·0	147·6	+3·2
35	Dichlorobromomethane.	$CHCl_2Br$	W. & S.	196·8	198·5	+0·4
36	Acetylene tetrachloride.	$C_2H_2Cl_4$	,,	259·0	261·0	+0·8
37	Acetylene tetrabromide.	$C_2H_2Br_4$	,,	311·0	315·8	+1·5
	,, ,,	,,	H. C. & R.	309·8	,,	+1·9
38	Ethylene dichloride.	$C_2H_4Cl_2$	Sch.	189·3	186·6	−1·4
	,, ,,	,,	M. & D.	189·1	,,	−1·3
39	Ethylidene dichloride.	,,	Sch.	188·5	,,	−1·0
	,, ,,	,,	M. & D.	188·6	,,	−1·1
40	Ethylene dibromide.	$C_2H_4Br_2$	M. & T.	215·7	214·0	−0·8
	,, ,,	,,	H. C. & R.	215·1	,,	−0·5

Halogen Derivatives (*continued*).

No.	Substance.	Formula.	Observer.	*P* obs.	*P* calc.	% Diff.
41	Ethyl bromide.	C_2H_5Br	„	167·6	163·1	−2·7
42	*n*-Propyl chloride.	C_3H_7Cl	Sch.	190·2	188·4	−0·9
43	*iso*Amyl chloride.	$C_5H_{11}Cl$	H. C. & R.	269·8	266·4	−1·3
44	*p*-Dichlorobenzene.	$C_6H_4Cl_2$	S.	279·5	281·5	+0·7
45	Fluorobenzene.	C_6H_5F	M. & D.	214·3	215·7	+0·5
46	Chlorobenzene.	C_6H_5Cl	R. & S.	244·5	244·3	−0·1
	„	„	M. & T.	244·9	„	−0·3
	„	„	H. C. & R.	243·9	„	+0·2
47	Bromobenzene.	C_6H_5Br	S.	260·6	258·0	−1·0
	„	„	M. & D.	258·0	„	±0·0
48	Iodobenzene.	C_6H_5I	S.	282·3	281·0	−0·5
	„	„	M. & D.	280·7	„	+0·1
49	*p*-Chlorobromobenzene.	C_6H_4ClBr	S	292·5	295·2	+0·9
50	*p*-Chloroiodobenzene.	C_6H_4ClI	„	316·4	318·2	+0·6
51	*p*-Chlorotoluene.	C_7H_7Cl	„	283·6	283·3	−0·1
52	*p*-Bromotoluene.	C_7H_7Br	„	296·8	297·0	+0·1
53	*p*-Iodotoluene.	C_7H_7I	„	318·6	320·0	+0·5

The deviations in this series are rather larger than those found with the hydrocarbons. There is some evidence for contraction in volume when two or more halogen atoms are attached to the same carbon atom. Thus the chlorine in carbon tetrachloride has a parachor of 53·8, while in propyl chloride the value obtained is 55·1 and in *iso*amyl chloride 56·7; on the other hand, chlorobenzene gives the normal value 54·5.

Ethers, etc.

No.	Substance.	Formula.	Observer.	*P* obs.	*P* calc.	% Diff.
54	Diethyl ether.	$C_4H_{10}O$	R. & S.	211·7	210·2	−0·7
	„ „	„	Sch.	211·9	„	−0·8
	„ „	„	M. & T.	209·5	„	+0·3
55	Dimethyl acetal.	$C_4H_{10}O_2$	Sch.	226·0	230·2	+1·4
56	Ethyl propyl ether.	$C_5H_{12}O$	M. & S.	252·0	249·2	−1·1
57	Paracetaldehyde.	$C_6H_{12}O_3$	Sch.	299·0	300·1	+0·4
	„	„	M. & S.	298·5	„	+0·5
58	Diethyl acetal.	$C_6H_{14}O_2$	Sch.	306·9	308·2	+0·4
59	Anisole.	C_7H_8O	W. & S.	265·6	266·1	+0·2
	„	„	R. & G.	265·7	„	+0·2
	„	„	M. & T.	265·6	„	+0·2
	„	„	H. C. & R.	265·2	„	+0·3
60	Phenetole.	$C_8H_{10}O$	R. & G.	303·5	305·1	+0·5
	„	„	M. & T.	303·6	„	+0·5
	„	„	H. C. & R.	302·8	„	+0·8
61	Anethole.	$C_{10}H_{12}O$	M. & S.	363·2	372·1	+2·5

With the exception of anethole the agreement in this series is good and establishes the value 20·0 for oxygen. The figures for paracetaldehyde are of interest, since they confirm the cyclic structure. The " calculated " parachor is obtained by adding to the sum of the atomic parachors for this substance the constant for a six-membered ring; if one only of the oxygen atoms were doubly linked, a much larger molecular parachor should be found.

Aldehydes and Ketones.

No.	Substance.	Formula.	Observer.	*P* obs.	*P* calc.	% Diff.
62	Acetone.	C_3H_6O	R. & G.	161·7	160·2	−0·9
	,,	,,	Sch.	162·0	,,	−1·1
	,,	,,	M. & O.	160·9	,,	−0·4
63	*aa*-Dichloroacetone.	$C_3H_4OCl_2$	H. C. & R.	244·1	234·6	−4·2
64	Monochloroacetone.	C_3H_5OCl	,,	192·7	197·4	+2·4
65	Methyl ethyl ketone.	C_4H_8O	M. & O.	198·2	199·2	+0·5
66	Furfural.	$C_5H_4O_2$	M. & S.	212·9	210·5	−1·2
67	Acetylacetone.	$C_5H_8O_2$	M. & C.	240·7	247·2	+2·6
68	Diethyl ketone.	$C_5H_{10}O$	M. & O.	236·2	238·2	+0·9
69	Methyl propyl ketone.	,,	R. & G.	233·0	,,	−2·3
	,, ,,	,,	M. & S.	238·0	,,	+0·1
70	Benzaldehyde.	C_7H_6O	M. & O.	256·2	255·1	−0·4
	,,	,,	H. C. & R.	254·0	,,	+0·4
71	Dipropyl ketone.	$C_7H_{14}O$	M. & K.	314·1	316·2	+0·7
72	Acetophenone.	C_8H_8O	M. & S.	293·8	294·1	+0·1
73	Methyl hexyl ketone.	$C_8H_{16}O$	M. & O.	355·7	355·2	−0·1
74	Benzophenone.	$C_{13}H_{10}O$	W. & S.	428·2	428·0	−0·1
	,,	,,	M. & S.	425·2	,,	+0·6

Serious deviations are found only for acetylacetone and the chlorinated acetones. Since in the latter the differences are opposite in sign in the two compounds investigated, it would seem probable that they are due to experimental error. The value deduced for carbonyl oxygen from the ten remaining compounds is exactly equal to the sum of the constant for a double bond and that for oxygen in the ethers.

Esters.

No.	Substance.	Formula.	Observer.	*P* obs.	*P* calc.	% Diff.
75	Methyl formate.	$C_2H_4O_2$	R. & S.	138·6	138·0	−0·5
	,, ,,	,,	M. & Sch.	137·7	,,	+0·2
76	Ethyl formate.	$C_3H_6O_2$	Sch.	178·4	177·0	−0·8
	,, ,,	,,	M. & Sch.	177·0	,,	±0·0
77	Methyl acetate.	,,	Sch.	177·2	,,	−0·1
	,, ,,	,,	M. & Sch.	176·7	,,	+0·2
78	*n*-Propyl formate.	$C_4H_8O_2$	Sch.	224·4	216·0	−3·6
	,, ,,	,,	M. & Sch.	216·1	,,	−0·1
79	Ethyl acetate.	,,	R. & S.	217·1	,,	−0·5
	,, ,,	,,	Sch.	217·8	,,	−0·9
	,, ,,	,,	M. & Sch.	215·6	,,	+0·2
80	Methyl propionate.	,,	Sch.	215·1	,,	+0·4
	,, ,,	,,	M. & Sch.	214·9	,,	+0·5
81	*iso*Butyl formate.	$C_5H_{10}O_2$	Sch.	262·4	255·0	−2·9
82	*n*-Propyl acetate.	,,	,,	257·1	,,	−0·8
	,, ,,	,,	M. & Sch.	255·0	,,	±0·0
83	Ethyl propionate.	,,	Sch.	255·2	,,	−0·1
	,, ,,	,,	M. & Sch.	254·4	,,	+0·2
84	Methyl butyrate.	,,	Sch.	254·1	,,	+0·4
	,, ,,	,,	M. & Sch.	254·3	,,	+0·3
85	Methyl *iso*butyrate.	,,	Sch.	253·1	,,	+0·8
	,, ,,	,,	M. & Sch.	253·5	,,	+0·6
86	Diethyl oxalate.	$C_6H_{10}O_4$	M. & C.	323·4	319·8	−1·1
87	*iso*Amyl formate.	$C_6H_{12}O_2$	Sch.	303·8	294·0	−3·3
	,, ,,	,,	M. & Sch.	293·7	,,	+0·1
	,, ,,	,,	M. & K.	293·6	,,	+0·1
88	*iso*Butyl acetate.	,,	Sch.	300·0	,,	−2·0
	,, ,,	,,	M. & D.	295·1	,,	−0·4

Esters (*continued*).

No.	Substance.	Formula.	Observer.	*P* obs.	*P* calc.	% Diff.
89	*n*-Propyl propionate.	„	Sch.	295·3	„	−0·4
90	Ethyl butyrate.	„	„	293·9	„	+0·1
	„ „	„	M. & T.	293·0	„	+0·3
	„ „	„	R. & Co.	294·2	„	−0·1
91	Ethyl *iso*butyrate.	„	Sch.	292·9	„	+0·4
92	Methyl valerate.	„	„	292·5	„	+0·5
93	Diethyl malonate.	$C_7H_{12}O_4$	M. & C.	362·0	358·8	−0·9
94	*iso*Amyl acetate.	$C_7H_{14}O_2$	Sch.	337·1	333·0	−1·2
	„ „	„	M. & O.	331·6	„	+0·4
95	*iso*Butyl propionate.	„	Sch.	331·8	„	+0·4
96	*n*-Propyl butyrate.	„	„	333·8	„	−0·3
97	*n*-Propyl *iso*butyrate.	„	„	332·6	„	+0·1
98	Ethyl valerate.	„	„	332·1	„	+0·3
99	Ethyl *iso*valerate.	„	H. C. & R.	331·9	„	+0·3
100	*iso*Amyl trichloro-acetate.	$C_7H_{11}O_2Cl_3$	M. & K.	443·0	444·6	+0·4
101	Ethyl maleate.	$C_8H_{12}O_4$	W. & S.	387·0	386·8	−0·1
102	Ethyl fumarate.	„	„	391·2	„	−1·1
	„ „	„	M. & K.	392·4	„	−1·4
103	Ethyl dimethylaceto-acetate.	$C_8H_{14}O_3$	M. & C.	382·3	381·0	−0·3
104	*iso*Amyl propionate.	$C_8H_{16}O_2$	Sch.	372·1	372·0	−0·1
105	*iso*Butyl butyrate.	„	„	370·5	„	+0·4
106	*iso*Butyl *iso*butyrate.	„	„	371·8	„	+0·1
107	*n*-Propyl valerate.	„	„	371·9	„	+0·1
108	*iso*Amyl butyrate.	$C_9H_{18}O_2$	H. C. & R.	410·9	411·0	+0·1
	„ „	„	M. & K.	408·5	„	+0·6
109	*iso*Butyl valerate.	„	„	409·4	„	+0·4
110	Methyl cinnamate.	$C_{10}H_{10}O_2$	W. & S.	383·1	377·9	−1·4
	„ „	„	M. & C.	385·2	„	−1·9
111	Ethyl diethylaceto-acetate.	$C_{10}H_{18}O_3$	„	446·6	459·0	+2·7
112	Ethyl phenylpro-piolate.	$C_{11}H_{10}O_2$	W. & S.	375·2	406·1	+8·3
113	Ethyl cinnamate.	$C_{11}H_{12}O_2$	M. & C.	417·2	416·9	−0·1
114	Propyl phenylpro-pionate.	$C_{12}H_{16}O_2$	W. & S.	468·7	466·9	−0·4
115	*iso*Propyl phenylpro-pionate.	„	„	467·4	„	−0·1
116	*iso*Butyl phenylpro-piolate.	$C_{13}H_{14}O_2$	„	424·7	484·1	+14·0
117	Diamyl maleate.	$C_{14}H_{24}O_4$	„	613·6	620·8	+1·2
118	Diamyl succinate.	$C_{14}H_{26}O_4$	M. & C.	621·3	631·8	+1·7
119	Diethyl sebacate.	„	W. & S.	646·9	631·8	−2·3
120	Di*iso*amyl sebacate	$C_{20}H_{38}O_4$	„	877·0	865·8	−1·3
121	Amyl stearate.	$C_{23}H_{46}O_2$	M. & K.	974·2	957·0	−1·9
122	Tripalmitin.	$C_{54}H_{104}O_6$	W. & S.	2252	2218	−1·5
123	Tristearin.	$C_{57}H_{110}O_6$	„	2380	2335	−1·9

A large number of measurements have been made on esters and the data obtained show clearly how small is the effect of position isomerism on the magnitude of the parachor. In the table below it will be seen that the mean values of the " observed " constant for the esters $C_6H_{12}O_2$ (neglecting Schiff's figures for the acetate and formate which are not confirmed by later workers) are all close to the " calculated " figure 294·0.

Parachors for isomeric esters.

Ester.	Mean P obs.	Ester.	Mean P obs.
*iso*Amyl formate	293·6	Ethyl butyrate	293·6
*iso*Butyl acetate	295·1	Ethyl *iso*butyrate	292·9
n-Propyl propionate ...	295·3	Methyl valerate	292·5

The mean value for O_2 in the esters which have been measured by two or more workers is 60·0, while the sum of the values found for ethereal and ketonic oxygen is 63·2. This difference seems to indicate that in the carboxyl group there is some interaction between the two oxygen atoms, a view which has been suggested previously on chemical grounds and from a study of other physical properties (compare Smedley, J., 1909, **95**, 231).

The only notable differences found in this series occur with the esters of phenylpropiolic acid previously referred to and with some of the esters of high molecular weight which are difficult to purify.

Amines and Amides.

No.	Substance.	Formula.	Observer.	P obs.	P calc.	% Diff.
124	Acetamide.	C_2H_5ON	T. & M.	148·0	150·8	+1·9
125	*n*-Propylamine.	C_3H_9N	,,	178·5	180·9	+1·4
126	Propionamide.	C_3H_7ON	,,	181·2	189·8	+4·7
127	Phenylhydrazine.	$C_6H_8N_2$	,,	255·7	266·3	+4·1
	,, ,,	,,	M. & C.	255·9	,,	+4·0
128	Dipropylamine.	$C_6H_{15}N$	T. & M.	297·3	297·8	+0·2
129	Benzylamine.	C_7H_9N	,,	273·7	275·7	+0·8
130	Formanilide.	C_7H_7ON	,,	273·5	284·7	+4·1
131	Benzamide.	,,	,,	279·9	,,	+1·7
132	Salicylamide.	$C_7H_7O_2N$	,,	295·3	304·7	+3·1
133	Acetanilide.	C_8H_9ON	,,	321·8	323·7	+0·7
134	Phenylacetamide.	,,	,,	320·2	,,	+1·1
135	Tripropylamine.	$C_9H_{21}N$	,,	413·6	414·8	+0·3
136	Methylacetanilide.	$C_9H_{11}ON$	,,	354·2	362·7	+2·1
137	Ethylacetanilide.	$C_{10}H_{13}ON$	,,	398·5	401·7	+0·8
138	Diphenylamine.	$C_{12}H_{11}N$	,,	402·1	409·6	+1·9
139	Dibenzylamine.	$C_{14}H_{15}N$	,,	485·6	487·6	+0·4
140	Tribenzylamine.	$C_{21}H_{21}N$	,,	695·7	699·5	+0·5

There are several large discrepancies in this table, notably amongst the amides, and it seems probable that the low figures observed may be due to the effect of association, which in other cases, for example, the alcohols, causes the observed parachor to be smaller than the predicted figure. Unfortunately, the only extended series of measurements available is that of Turner and Merry, who employed the method of capillary rise. New determinations of the surface tension and density of several substances belonging to this group are now in progress and will be discussed in a later communication.

Nitriles.

No.	Substance.	Formula.	Observer.	*P* obs.	*P* calc.	% Diff.
141	Acetonitrile.	C_2H_3N	M. & C.	122·2	120·0	−1·8
142	Butyronitrile.	C_4H_7N	H. C. & R.	201·2	198·0	−1·6
	,,	,,	T. & M.	198·9	,,	−0·5
	,,	,,	M. & C.	199·7	,,	−0·9
143	Valeronitrile.	C_5H_9N	,,	236·6	237·0	+0·2
144	*iso*Valeronitrile.	,,	H. C. & R.	237·3	,,	−0·1
145	*iso*Butylacetonitrile.	$C_6H_{11}N$	T. & M.	275·0	276·0	+0·4
146	Benzonitrile.	C_7H_5N	M. & T.	259·3	253·9	−2·1
	,,	,,	T. & M.	258·0	,,	−1·8
	,,	,,	M. & C.	255·5	,,	−0·8
147	Phenylacetonitrile.	C_8H_7N	T. & M.	293·6	292·9	−0·2
	,,	,,	M. & O.	293·4	,,	−0·2
148	*o*-Toluonitrile.	,,	T. & M.	292·5	,,	+0·2
	,,	,,	M. & C.	292·9	,,	±0·0
149	*m*-Toluonitrile.	,,	T. & M.	280·0	,,	+4·6
	,,	,,	M. & C.	280·7	,,	+4·4
150	*p*-Toluonitrile.	,,	T. & M.	295·2	,,	−0·8
	,,	,,	M. & C.	295·9	,,	−1·0

The constant for the CN group is taken as the sum of the values for carbon, hydrogen, and the triple bond, and good agreement is found except in the case of *m*-toluonitrile. Morgan and Chazal have confirmed the surface tensions found by Turner and Merry for this substance, but did not make new measurements of the density. In aliphatic compounds position isomerism does not have an appreciable effect upon the parachor and the constants for the three xylenes (15, 16, and 17) and the three nitrotoluenes (155, 156, and 157) do not exhibit any marked differences between the ortho-, meta-, and para-isomerides; hence it seems probable that Turner and Merry's densities for *m*-toluonitrile are too high. New measurements on this substance will be made shortly.

Nitro-compounds.

No.	Substance.	Formula.	Observer.	*P*. obs.	*P*. calc.	% Diff.
151	Nitromethane.	CH_3O_2N	H. C. & R.	132·1	131·1	−0·8
	,,	,,	M. & S.	132·0	,,	−0·7
152	Ethyl nitrate	$C_2H_5O_3N$	,,	189·6	190·1	+0·3
153	Nitrobenzene	$C_6H_5O_2N$	S.	264·5	265·0	+0·2
	,,	,,	M. & O.	264·1	,,	+0·3
	,,	,,	H. C. & R.	262·5	,,	+0·9
154	*p*-Nitrochlorobenzene	$C_6H_4O_2NCl$	S.	300·0	302·2	+0·7
155	*o*-Nitrotoluene.	$C_7H_7O_2N$	H. C. & R.	297·7	304·0	+2·1
156	*m*- ,,	,,	,,	297·0	,,	+2·3
157	*p*- ,,	,,	S.	302·8	,,	+0·4

The seven nitro-compounds tabulated give a mean value for the parachor for the nitro-group of 75·0. If the nitro-group has the structure $-N\lessdot^{O}_{O}$, the predicted constant is 98·9 or the sum of the values for N, 2O, and two double bonds. This value is based on the observation that in nitroso-compounds (159 160, 162, 165) the

double bond between nitrogen and oxygen has approximately the same value as that between carbon and carbon and between carbon and oxygen. Hence it appears very unlikely that the nitro-group contains two doubly bound oxygen atoms. The alternative cyclic formula $—N\begin{matrix}O\\|\\O\end{matrix}$ is advocated by Brühl to account for the refractivity of nitro-compounds (*Z. physikal. Chem.*, 1898, **25**, 577). If this is taken as the true structure, the constant for a three-membered ring is 22·5, which is a little less than that for a double bond. Measurements on *cyclo*propane derivatives are now being made to obtain a further value for this constant. It will be seen that the same value for the nitro-group serves to reproduce the experimental figures for both aliphatic and aromatic nitro-compounds and for ethyl nitrate.

Miscellaneous.

No.	Substance.	Formula.	Observer.	*P* obs.	*P* calc.	% Diff.
158	Hydrogen peroxide.	H_2O_2	M. & H.	69·6	74·2	−6·6
159	Nitrosyl chloride.	NOCl	B. & P.	108·1	110·0	−1·7
160	Dimethylnitrosoamine	$C_2H_6ON_2$	M. & S.	183·8	180·4	−1·9
,,	,,	,,	T. & M.	184·8	,,	−2·4
161	Ethyl carbamate.	$C_3H_7O_2N$	,,	202·2	209·8	−3·8
162	Diethylnitrosoamine.	$C_4H_{10}ON_2$	,,	260·3	258·4	−0·7
163	Pyridine.	$C_5H_{11}N$	M. & T.	199·8	197·7	−1·1
164	Piperidine.	$C_5H_{11}N$	M. & O.	231·5	230·7	−0·4
165	Phenylmethylnitrosoamine.	$C_7H_8ON_2$	T. & M.	313·6	314·6	+0·3
166	Quinoline.	C_9H_7N	M. & T.	306·4	303·6	−0·9
167	Ethyl phenylcarbamate.	$C_9H_{11}O_2N$	T. & M.	375·6	382·7	+1·9

The figures for hydrogen peroxide are of interest, since they seem to favour the formula HO·OH for this substance. Hydrogen peroxide is associated in the liquid state, and for other associated substances the observed parachor is less than the predicted value but increases steadily with temperature and approaches the latter figure in the neighbourhood of the critical temperature. Hence the observed figure of 69·6 is quite compatible with the parachor of 74·2 calculated for the above formula. No compounds containing quadrivalent oxygen have yet been examined, but unless the parachor for such oxygen is very much smaller than that for the bivalent element the molecular constant for the formula $H_2O{:}O$ cannot be much smaller than 97·4, a figure which is far too high to account for the observed constant.

The significance of the data for nitroso-compounds has already been considered. Pyridine and piperidine give approximately the same value for the six-membered ring constant as do benzene and *cyclo*hexane derivatives, while the double ring in quinoline seems to have twice this value.

The parachors for 167 compounds are collected in the preceding tables and of these 145 are within 2 per cent., and 104 within 1 per cent. of the predicted figures. In the case of 45 compounds concordant measurements of surface tension and density have been made by two or more independent workers; of these, all the parachors are within 2 per cent. and 36 within 1 per cent. of the calculated values.

A few figures are available for the surface tensions and densities of free elements; in the following table the observed parachors are compared with those to be expected from the constants deduced from organic compounds.

Element.	Formula.	*P* obs.	*P* calc.	Observer.
Hydrogen	H·H	35·2	34·2	K. O.
Chlorine	Cl·Cl	111·5	108·3	M.
Bromine	Br·Br	132·1	136·0	M. & D.
Oxygen	O:O	54·0	63·2	B. & D.
Nitrogen	N:N	60·4	71·6	,,

The agreement is fair for the three univalent elements, but large differences are found for oxygen and nitrogen.

The references to the papers from which the data discussed in the present communication were obtained are collected together below. In all cases the figure quoted for the parachor is the average of the values found for the temperature range which had been investigated. Corrections have been applied to some of the surface tension data; those necessary for the observations of Ramsay and Shields and of Walden and Swinne have been discussed in a previous communication (this vol., p. 32). Schiff measured the difference in height of the meniscuses in two narrow communicating tubes; a few of his data were recalculated by means of the theory of the method of capillary rise (J., 1921, **119**, 1483), and his corrections, which depended on measurements of the dimensions of the meniscus, were found to be substantially valid. Renard and Guye also employed the method of capillary rise and adopted Ramsay and Shields's figures for benzene as standards. The figures found by these workers were therefore corrected in the same manner as those of Walden and Swinne. Morgan and his co-workers used the drop-weight method and assumed that within certain limits the weight of a drop from a given tip is proportional to the surface tension. They used benzene as standard liquid, but adopted a value for its surface tension which is 3 per cent. lower than that found by later workers. Their observations have therefore been recalculated, using the higher values for benzene (this vol., p. 31) and applying the corrections for the drop-weight method which have been worked out by Harkins and Brown (*J. Amer. Chem. Soc.*, 1919, **41**, 499).

References.

B. & D.	Baly and Donnan, J., 1902, **81**, 907.
B. & P.	Briner and Pylkoff, *J. Chim. Phys.*, 1912, **10**, 657.
H. C. & R.	Harkins, Clark, and Roberts, *J. Amer. Chem. Soc.*, 1920, **42**, 700.
H. & E.	Harkins and Ewing, *ibid.*, 1919, **41**, 1977.
K.	Kistiakowski, *Ann. Inst. Polytech. Petrograd*, 1904, **1**, 450.
K. & K.	Kremers and Kremers, *J. Amer. Pharm. Assoc.*, 1920, **9**, 860.
K. O.	Kammerlingh Onnes, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 528.
M.	Marchand, *J. Chim. Phys.*, 1913, **11**, 574.
M. & C.	Morgan and Chazal, *J. Amer. Chem. Soc.*, 1913, **35**, 1821.
M. & D.	Morgan and Daghlien, *ibid.*, 1911, **33**, 657.
M. & K.	Morgan and Kramer, *ibid.*, 1913, **35**, 1834.
M. & O.	Morgan and Owen, *ibid.*, 1911, **33**, 1713.
M. & Sch.	Morgan and Schwarz, *ibid.*, p. 1041.
M. & S.	Morgan and Stone, *ibid.*, 1913, **35**, 1505.
M. & T.	Morgan and Thomssen, *ibid.*, 1911, **33**, 657.
M. & H.	Maass and Hatcher, *ibid.*, 1920, **42**, 2562.
M. & W.	Maass and Wright, *ibid.*, 1921, **43**, 1098.
R. & C.	Richards and Carver, *ibid.*, p. 827.
R. & Co.	Richards and Coombs, *ibid.*, 1915, **37**, 1656.
R. & G.	Renard and Guye, *J. Chim. Phys.*, 1915, **5**, 81.
R. & S.	Ramsay and Shields, *Phil. Trans.*, 1893, **184**, 647.
Sch.	Schiff, *Annalen*, 1884, **223**, 47.
S.	Sugden, this vol., pp. 32, 1167.
T. & M.	Turner and Merry, J., 1910, **97**, 2068.
W. & S.	Walden and Swinne, *Z. physikal. Chem.*, 1912, **79**, 700.

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CXLIII.—*Conductivity and Ionisation of Solutions of Potassium Iodide in Nitromethane.*

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IN recent years, numerous investigations have been carried out bearing on the conductivity of non-aqueous solutions, Walden in particular being responsible for the collection and correlation of data in this field. As is well known, he has succeeded in deducing various interesting relationships between conductivity and ionisation on the one hand, and the physical properties (notably viscosity and specific inductive capacity) of the solvent on the other.

In spite of this accumulation of data and the generalisations which have followed, there are yet many points which await settlement, and there is still room for accurate measurements of the conductivity of non-aqueous solutions. Apart from the noteworthy discrepancies between the results of different observers, there is the fundamental problem of the calculation of Λ_∞ from the values of Λ. The best method of solving this problem is by no means clear, as will appear later, although some of Walden's most recent studies seem to provide a practical foundation for the necessary extrapolation.

The object of the present investigation, however, was not so much to study the different methods of extrapolation as to provide accurate conductivity values for a given solute in a given solvent over a wider range of temperature than has usually been employed with organic solvents. Solutions of potassium iodide in nitromethane have accordingly been examined in detail at the following six temperatures :—0°, 25°, 40°, 55°, 70°, 85°, and up to the dilution $V = 10{,}000$.

From the values of Λ recorded for each temperature, the figure for Λ_∞ was deduced by Washburn's method (*J. Amer. Chem. Soc.*, 1918, **40**, 122), that is, the value of the mass action expression $\Lambda^2/\Lambda_\infty(\Lambda_\infty - \Lambda)V$ was plotted against the concentration for various assumed values of Λ_∞, and that figure for Λ_∞ was adopted as the most probable which led to no abrupt rise or fall in the curve at the highest dilutions. The data obtained in the present investigation have been used also to test the cube-root linear extrapolation formula frequently employed until recently by Walden and others (see, for example, Philip and Courtman, J., 1910, **97**, 1261), but it is found that the Λ–$\sqrt[3]{c}$ curve at very low concentrations begins to be distinctly concave to the $\sqrt[3]{c}$ axis. When Λ is plotted against either $c^{0{\cdot}5}$ or $c^{0{\cdot}45}$ (see Lorenz, *Z. anorg. Chem.*, 1919, **108**, 191; Walden, *ibid.*, 1920, **115**, 49), a much closer approximation to a straight line is obtained, and it is instructive to compare the values of Λ_∞ based on the graphical extrapolation of these lines with the values deduced by Washburn's method. At each temperature, the figure obtained by Washburn's method is 1—3 per cent. lower than that based on the $c^{0{\cdot}5}$ line.

With the values of Λ_∞ deduced by the Washburn method, figures for $\alpha = \Lambda/\Lambda_\infty$ have been worked out for certain concentrations at the different temperatures. The results established quite definitely the conclusion that the degree of ionisation, as measured by the conductivity ratio, decreases with rising temperature, in agreement with what has been found for aqueous salt solutions.

Of interest also is the variation of Λ_∞ with temperature in

relation to the parallel increase of fluidity. The results go to show that the equivalent conductivity at infinite dilution is very nearly proportional to the fluidity (see p. 1195).

Experimental.

The source of alternating current was an audio-oscillator, operated by three accumulators. This instrument could be adjusted to give a fairly pure note with a frequency of about 800 per second, and was used in conjunction with a tuned telephone. A variable capacity was put in parallel with either the conductivity cell or the resistance box, according to the concentration of the solution in the cell and the resistance in the box. Subject to suitable adjustment of this capacity, a sharp setting, marked by complete silence in the telephone, was always obtained even with the solutions of highest resistance.

The cell was a stoppered, round-bottomed, glass bottle of about 20 c.c. capacity, the electrodes—two platinum disks 0·8 cm. in diameter and 0·4 cm. apart—being sealed in through the sides. The electrodes had previously been sand-blasted, coated with platinum black, and then strongly heated. The cell constant, determined by measurements at 25°, was taken to be the same for all temperatures between 0° and 85°, since it was estimated that the change in the effective dimensions of the conducting column within that range was negligible.

After preliminary trials had shown that the preparation and dilution of the solutions by transference of known volumes was unsatisfactory, the method of making the solutions by weight was adopted in all cases. The procedure was to prepare, by weighing both salt and nitromethane, about 100 c.c. of approximately $N/100$-potassium iodide. One portion of this was used for the conductivity measurement and then discarded, whilst another portion was transferred to a weighed flask containing a weighed quantity of nitromethane. A portion of the diluted solution thus prepared was taken for a conductivity measurement, and the process just outlined was repeated until the practicable limit of dilution was reached, that is, about $V = 10{,}000$. Measurements on at least two series of solutions were made at each temperature, and in view of the very good agreement usually obtained further repetition was deemed unnecessary, except in one or two cases. In order to deduce the volume concentrations of the solutions, density determinations were made with $N/100$- and $N/200$-potassium iodide as well as with the pure solvent nitromethane.

The nitromethane obtained from the makers, after standing over calcium chloride for a fortnight and being distilled twice, gave

$\kappa = 0{\cdot}7 \times 10^{-6}$ at 25°. A further distillation under reduced pressure effected a distinct improvement, giving a product with $\kappa = 0{\cdot}4 \times 10^{-6}$, and this was the conductivity of the material employed in the measurements. Between each series of experiments the nitromethane was distilled from the potassium iodide, stirred for 2 or 3 days with calcium chloride, and then redistilled under reduced pressure. The solvent correction at $V = 10{,}000$ was about 3·5 per cent.

The potassium iodide used in the investigation was of A.R. quality, and was dried over phosphorus pentoxide before use. The conductivity of its $N/100$-aqueous solution was found to be in excellent agreement with the results of various investigators quoted by Bray and MacKay (*J. Amer. Chem. Soc.*, 1910, **32**, 918).

The viscosity measurements were carried out with an Ostwald viscosimeter. The times of flow were repeatedly determined both for water and for nitromethane at all the experimental temperatures, the minimum time of flow being 300 seconds. A correction for the change in effective head due to change in the total volume of the liquid with temperature was applied, and found to amount at 85° to 0·4 per cent. for water and to 1·5 per cent. for nitromethane. The values of the fluidity of nitromethane were calculated from Thorpe and Rodger's figures for the viscosity of water.

The results of the conductivity measurements carried out at the various temperatures are recorded in Table I.

The values of Λ_∞ for each temperature obtained by Washburn's method appear in Table I, but it is desirable to collect them and to study their relation to the temperature, as well as to the values for Λ_∞ deduced in other ways. As already indicated on p. 1190, a figure for the maximum limit of the equivalent conductivity can be obtained by plotting Λ against $c^{0{\cdot}5}$ or $c^{0{\cdot}45}$, and drawing in each case a straight line as nearly as possible through the experimental points. The values of Λ_∞ based on the extrapolation of the respective straight lines are recorded in the third and fourth columns of Table II.

When the figures recorded in the second column of Table II are plotted against the temperature, the curve obtained is slightly convex to the temperature axis. The values of Λ_∞ for 0°, 25°, 40°, 55°, and 85° lie well on the curve, but the value for 70° (*i.e.*, 191·1) is distinctly above it, and is probably 1—2 units too high. An examination of the figures for Λ at 70°, recorded in Table I, indicates that the value found for the most dilute solution examined at that temperature is almost certainly in error, and this is the probable explanation of the unsatisfactory value obtained for Λ_∞ by the Washburn method in this case.

TABLE I.

Dilution V litres.	Conductivity. $\kappa \times 10^6$.	Λ.	Dilution V litres.	Conductivity. $\kappa \times 10^6$.	Λ.
	0°.			25°.	
92·50	717·0	66·32	82·90	1027	85·14
207·7	358·0	74·36	111·9	802·9	89·84
402·2	197·2	79·32	200·9	488·6	98·06
792·3	104·8	83·08	267·1	380·7	101·57
1129	74·78	84·45	408·0	259·0	105·5
2382	36·38	86·67	740·2	150·6	111·17
4136	21·18	87·60	1673	69·65	115·82
9243	9·613	88·86	4915	24·70	119·27
[∞	0·31	90·20]	10,082	12·38	120·47
			[∞	0·43	121·8]
	40°.			55°.	
97·26	1035·0	101·0	100·12	1144·0	114·54
219·3	524·8	115·1	223·8	584·0	130·70
424·6	292·2	124·0	435·6	327·4	142·60
836·5	156·6	131·0	858·1	175·6	150·70
1192	111·9	133·3	1222·7	125·5	153·50
2515	54·62	137·2	2579	61·43	158·44
4365	31·88	139·2	4478	35·75	160·11
9756	14·46	141·1	10,008	16·24	162·57
[∞	0·45	143·0]	[∞	0·51	164·8]
	70°.			85°.	
106·8	1212·0	129·2	106·60	1304	143·25
168·6	840·1	141·4	173·3	905·7	157·0
228·0	649·9	148·2	235·05	703·7	165·4
514·6	319·0	164·2	530·4	346·9	184·0
847·6	202·4	171·5	875·4	220·5	193·0
1323·0	132·6	176·2	1370·0	145·0	198·7
2412	75·20	181·5	2492	82·20	204·8
3157	57·66	182·0	3234	63·05	205·9
10,537	17·82	187·8	10,860	10·37	210·4
[∞	0·62	191·1]	[∞	0·74	213·4]

TABLE II.

Temp.	Values of Λ_∞. By Washburn's method.	From Λ and $c^{0·5}$.	From Λ and $c^{0·45}$.
0°	90·2	91·3	92·4
25	121·8	123·8	125·8
40	143·0	145·6	147·2
55	164·8	169·4	171·3
70	191·1	194·4	197·0
85	213·4	218·1	223·2

In order to arrive at comparative figures for the influence of temperature on (1) the conductivity of the dilute solutions, and (2) the degree of ionisation, the experimental values of Λ, as recorded in Table I, were plotted against the cube root of the concentration, and from the curve so obtained (practically a straight line up to $V = 1000$) the values of Λ corresponding with $V = 100$ and $V = 800$ were read off for each temperature.

TABLE III.

Interpolated Values of Λ.

	0°.	25°.	40°.	55°.	70°.	85°.
$V = 100$	67·2	88·1	101·7	114·5	127·3	140·3
$V = 800$	83·1	111·6	130·6	150·0	170·7	191·4

The influence of temperature on conductivity for the cases $V = 100$, $V = 800$, and $V = \infty$ may be conveniently represented by taking the value of Λ at 0° in each case as unity, and setting out the relative values at the other temperatures. This is done in Table IV.

TABLE IV.

Values of $\frac{\Lambda \text{ at } t°}{\Lambda \text{ at } 0°}$.

Temperature.	$V = 100$.	$V = 800$.	$V = \infty$.
0°	1·000	1·000	1·000
25	1·310	1·343	1·350
40	1·512	1·572	1·585
55	1·704	1·806	1·827
70	1·894	2·055	2·109
85	2·087	2·305	2·366

An inspection of these figures shows that the temperature coefficient of the conductivity increases with the dilution, being about 0·013 for a $N/100$-solution, and 0·014—0·015 for a $N/800$-solution.

The influence of temperature on the degree of ionisation can be deduced by combining the values of Λ set out in Table III with the values of Λ_∞ recorded in the second column of Table II. The degrees of ionisation at the two concentrations in question and the six experimental temperatures, given by $\alpha = \Lambda/\Lambda_\infty$, are tabulated below:

TABLE V.

Degree of Ionisation at Different Temperatures.

	0°.	25°.	40°.	55°.	70°.	85°.
$V = 100$	0·745	0·723	0·711	0·695	0·676	0·658
$V = 800$	0·921	0·917	0·913	0·910	0·907	0·897

These figures show clearly that the degree of ionisation diminishes steadily with rising temperature.

As stated on p. 1192, the viscosity of pure nitromethane was determined at the same temperatures as those at which the conductivity of the potassium iodide solutions was measured. From the figures for the viscosity (η) the values of the fluidity ($f = 1/\eta$) were calculated, as recorded in Table VI, which includes also figures for the density of nitromethane:

TABLE VI.

Temperature	0°	25°	40°	55°	70°	85°
Density	1·1654	1·1300	1·1042	1·0764	1·0474	1·0164
Fluidity (f)	118·6	158·3	190·0	222·2	254·8	291·8

When log Λ_∞ is plotted against log f, Λ_∞ and f being corresponding values of the conductivity and the fluidity respectively at the different temperatures, the points are found to lie very nearly on a straight line. From the slope of this line it can be shown that, whilst the value of Λ_∞ is approximately proportional to f, the exact relationship between these quantities for the range 0—85° is given by the equation $\Lambda_\infty = k.f^{0\cdot95}$, where k is a constant (compare Johnston, *J. Amer. Chem. Soc.*, 1909, **31**, 1010).

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
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CXLIV.—*Nitrogen Chlorides derived from Nitro-substituted Acetanilides.*

By FREDERICK DANIEL CHATTAWAY and HENRY JAMES DOWDEN.

IT is well known that the intramolecular change whereby a halogen atom migrates from the nitrogen atom of a *N*-halogenoacetanilide to the nucleus proceeds less and less readily as the number of halogen atoms in the molecule increases. Migration is also hindered or, in the case of the ortho-substituted compound, prevented by the presence of a nitro-group in the nucleus.

In this paper is described the behaviour of the *N*-chloro-derivatives of nitroacetanilides containing more than one nitro-group. In no case does migration occur under the conditions employed; either the *N*-chloro-derivative undergoes hydrolysis and decomposition or the original nitroacetanilide is reformed.

In the case of *N*-chloro-2- and -3-nitroaceto-*p*-toluidides the effect of the nitro-group is very greatly to hinder transformation.

2 : 4 : 6-Trinitroacetanilide, dissolved in acetic acid, is quite indifferent to chlorine, but in aqueous caustic potash it reacts with this agent to form N-*chloro*-2 : 4 : 6-*trinitroacetanilide*, which is a well-crystallised compound showing all the characteristic reactions of substituted nitrogen chlorides :

$$X\cdot NH\cdot COMe \longrightarrow X\cdot N{:}CMe\cdot OK \longrightarrow X\cdot NCl\cdot CMeCl\cdot OK \longrightarrow X\cdot NCl\cdot COMe. \quad [X = C_6H_2(NO_2)_3]$$

EXPERIMENTAL.

N-*Chloro*-2 : 4-*dinitroacetanilide*, $C_6H_3(NO_2)_2\cdot NClAc$.—A cooled solution of 5 grams of 2 : 4-dinitroacetanilide and 4 grams of

anhydrous sodium acetate in 25 c.c. of acetic acid was saturated with chlorine and poured over ice, when the chloroamino-derivative separated in oily drops, which solidified. It was recrystallised twice from light petroleum (b. p. 60—80°), in which it was sparingly soluble, separating in small, faintly yellow, rhombic prisms, m. p. 54—55° (Found: Cl = 13·68. $C_8H_6O_5N_3Cl$ requires Cl = 13·66 per cent.). When it was warmed with acetic acid or acetic acid containing a few drops of concentrated hydrochloric acid, chlorine was evolved and 2 : 4-dinitroacetanilide reformed. On heating it with the latter solvent in an atmosphere of chlorine in a sealed tube, much decomposition took place and a considerable quantity of 2 : 4-dinitroaniline was produced.

N : 6-*Dichloro*-2 : 4-*dinitroacetanilide*, $C_6H_2Cl(NO_2)_2{\cdot}NClAc$.—6-Chloro-2 : 4-dinitroaniline, m. p. 156°, prepared by the prolonged action of chlorine on an acetic acid solution of 2 : 4-dinitroaniline containing a considerable quantity of concentrated hydrochloric acid, was acetylated by warm acetic anhydride and a little concentrated sulphuric acid. The acetyl derivative crystallised from hot acetic acid in long, slender, almost colourless prisms, m. p. 221°. It was suspended in chloroform and shaken with hypochlorous acid. The chloroform solution was dried with calcium chloride, the solvent evaporated, and the residue, a yellow, viscid oil which slowly solidified, recrystallised from low-boiling petroleum, in which it was very sparingly soluble, the *N*-chloro-derivative separating in small, faintly yellow, rhombic prisms, m. p. 68·5° (Found: Cl = 11·95. $C_8H_5O_5N_3Cl_2$ requires Cl as NCl = 12·06 per cent.). When it was heated with acetic acid, chlorine was liberated and 6-chloro-2 : 4-dinitroacetanilide reformed.

N-*Chloro*-2 : 4 : 6-*trinitroacetanilide*, $C_6H_2(NO_2)_3{\cdot}NClAc$.—Picrylamine was prepared by a modification of Witt and Witte's method (*Ber.*, 1908, **41**, 3091), the temperature being allowed to rise to 25—30° during the addition of a cooled solution of 60 grams of potassium nitrate in 400 grams of concentrated sulphuric acid to a similarly cooled solution of 40 grams of *p*-nitroaniline in 400 grams of the same solvent; the yield was thereby improved.

A solution of 15 grams of picrylamine in 50 c.c. of hot acetic anhydride containing a few drops of concentrated sulphuric acid was heated to boiling and then cooled, when 2 : 4 : 6-trinitroacetanilide separated as a mass of minute needles; after being twice crystallised from acetic acid, it was practically pure, although still slightly yellow.

The very finely powdered acetyl compound (5 grams) was triturated with a cold solution of 2 grams of sodium hydroxide in 15 c.c. of water and filtered. Through the deep orange-red filtrate,

cooled by a freezing mixture, a rapid stream of chlorine was passed. As soon as the orange colour was discharged the solid that had separated was filtered off, washed with water, pressed between filter-paper, and dissolved in warm chloroform. The dried, filtered solution was concentrated to a small bulk and a little light petroleum added, when the chloroanilide separated as a colourless, crystalline solid. It was recrystallised from warm chloroform, in which it was readily soluble, separating in glistening, pale yellow, rhombic plates, m. p. 127·5° (the yield was usually 20 per cent. of the theoretical). It is essential that all the operations should be carried out as rapidly as possible, since the anilide when dissolved in caustic alkali very readily undergoes hydrolysis and since the chloroamino-compound is somewhat unstable in contact with moist solvents, although when pure and dry it can be kept in a desiccator for a considerable time without change (Found : Cl=11·72. $C_8H_5O_7N_4Cl$ requires Cl = 11·64 per cent.). On heating with glacial acetic acid, *N*-chloro-2 : 4 : 6-trinitroacetanilide decomposes, chlorine is liberated, and 2 : 4 : 6-trinitroacetanilide is to a large extent reformed.

N-*Chloro*-2-*nitroaceto*-p-*toluidide*, $NO_2{\cdot}C_6H_3Me{\cdot}NClAc$, was obtained by shaking 2-nitroaceto-*p*-toluidide, suspended in chloroform, with a solution of hypochlorous acid. It is easily soluble in warm chloroform, from which it separates in compact, faintly yellow, rhombic prisms, m. p. 125—126° (Found : Cl = 15·41. $C_9H_9O_3N_2Cl$ requires Cl = 15·51 per cent.). This compound is comparatively stable and can be recrystallised with only very slight decomposition from boiling acetic acid, from which it separates in a less compact habit in almost colourless, slender prisms. When it was heated with acetic acid containing a few drops of hydrochloric acid, chlorine was liberated and 2-nitroaceto-*p*-toluidide regenerated. When it was heated with glacial acetic acid in a sealed tube at 100°, only a tarry product was obtained, from which nothing definite could be isolated.

N-*Chloro*-3-*nitroaceto*-p-*toluidide*, similarly prepared from the 3-nitro-compound, is sparingly soluble in warm light petroleum and separates in glistening, faintly yellow, four-sided, rhombic plates, m. p. 51·5° (Found : Cl = 15·56. $C_9H_9O_3N_2Cl$ requires Cl = 15·51 per cent.). When warmed with acetic acid, it decomposed almost immediately, chlorine was liberated and 3-nitroaceto-*p*-toluidide was largely reproduced. When it was heated with acetic acid in a sealed tube, only tarry substances were formed.

THE QUEEN'S COLLEGE, OXFORD. [*Received, March 11th*, 1924.]

CXLV.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXI. The Chemical Significance of Rotatory Dispersion.*

By HAROLD HUNTER.

TEN years have elapsed since Lowry and Dickson (J., 1913, **103**, 1067) attempted to systematise our knowledge of the rotatory dispersion of organic compounds by dividing them into two classes; (*a*) those exhibiting a rotatory dispersive power which could be adequately expressed by one term of Drude's equation, $\alpha = \Sigma k_n/(\lambda^2 - \lambda_n^2)$,* and were said to show "simple" rotatory dispersion, and (*b*) those requiring more than one term of this equation (the methods of measurement at present available do not admit of the detection of more than two terms), which were said to exhibit "complex" rotatory dispersion. It has been found that most of the compounds so far examined belong to the former class, the majority of the exceptions being esters and acids.

It is the purpose of this paper to show that this classification is as yet of no practical value, since there is no method at present available for distinguishing with certainty between the two kinds of dispersion. It is submitted, in fact, that the test which has been proposed to differentiate simple from complex rotatory dispersion distinguishes actually, not between these two classes, but between "normal," and potentially "anomalous" rotatory dispersion. The term "normal" is applied to the rotatory dispersion of a compound when its rotatory power increases numerically with decreasing wave-length of light. The term "potentially anomalous," † on the other hand, is reserved for the rotatory dispersion of a compound when its rotatory power, between certain wave-lengths *on the greater wave-length side of that ultra-violet rotatory absorption band which is nearer the visible region of the spectrum*, decreases numerically with decreasing wave-length of light. The restriction in italics in the last sentence is necessary because all cases of complex rotatory

* Baly (*Chem. and Ind.*, 1924, **43**, 331) has suggested writing the Drude equation in the form $\alpha = \Sigma c_n/(\nu_n^2 - \nu^2)$, in order to emphasise its connexion with the Sellmeier equation. It is submitted that this connexion is well brought out by writing the latter in the form employed in Part XIX of this series of investigations (J., 1923, **123**, 434), and that, further, the form suggested by Baly suffers from the drawback that it makes c_n dependent on ν and ν_n.

† The term "potentially anomalous" should be read to include the class "actually anomalous." In curve IVa, Fig. 1, for example, the anomaly is bound to appear somewhere to the right of λ_0^2: in the V region it is "potential," in the G region it is "actual."

dispersion must become anomalous between certain limits of wavelength, but the only case which can be detected at present is that in which the anomaly appears for values of λ greater than that of the ultra-violet absorption band affecting the rotation and which is nearest the visible region of the spectrum.

The method at present adopted for distinguishing between simple and complex rotatory dispersion is a graphical one, which involves plotting $1/\alpha$ against λ^2. A one-term Drude equation leads to a linear relationship between these variables, whilst it is claimed that a two-term equation should not. This claim should, however, be examined a little more in detail. Consider the equation

$$\alpha = \frac{k_0}{\lambda^2 - {\lambda_0}^2} + \frac{k_1}{\lambda^2 - {\lambda_1}^2}.$$

Then

$$\frac{1}{\alpha} = \frac{\lambda^4 - \lambda^2({\lambda_0}^2 + {\lambda_1}^2) + {\lambda_0}^2\,{\lambda_1}^2}{(k_0 + k_1)\lambda^2 - k_0{\lambda_1}^2 - k_1\,{\lambda_0}^2}.$$

Putting $\lambda^2 = x$; $1/\alpha = y$; ${\lambda_0}^2 + {\lambda_1}^2 = a$; ${\lambda_0}^2\,{\lambda_1}^2 = b$; $k_0 + k_1 = c$; and $k_0{\lambda_1}^2 + k_1{\lambda_0}^2 = d$

we get

$$y = \frac{x^2 - ax + b}{cx - d},$$

which may be written in the form

$$y = \frac{x}{c} + \frac{d - ac}{c^2} + \frac{b + \dfrac{d^2 - acd}{c^2}}{cx - d}$$

which is the equation to a hyperbola. By inspection, it follows that

(*a*) y is infinite only when the third term is infinite, *i. e.*, when $cx - d = 0$, or $x = d/c$, and

(*b*) the equation is linear in x only when the third term is zero, *i.e.*, when (i) $b = (acd - d^2)/c^2$ or (ii) $cx - d$ is infinite.

Taking these conditions in turn, we find that

(*a*) $1/\alpha$ is infinite (or $\alpha = 0$), when $\lambda^2 = \dfrac{k_0{\lambda_1}^2 + k_1{\lambda_0}^2}{k_0 + k_1}$.

(*b*) the expression is linear in $1/\alpha$ and λ^2 when

(i) $${\lambda_0}^2{\lambda_1}^2 = \frac{({\lambda_0}^2 + {\lambda_1}^2)(k_0 + k_1)(k_0{\lambda_1}^2 + k_1{\lambda_0}^2) - k_0{\lambda_1}^2 - k_1{\lambda_0}^2}{(k_0 + k_1)^2}$$

which is satisfied if, and only if, $\lambda_0 = \lambda_1$ and

(ii) $\lambda^2(k_0 + k_1) - k_0{\lambda_1}^2 - k_1{\lambda_0}^2$ is infinite, *i.e.*, λ is infinite. The asymptotes to the hyperbola are

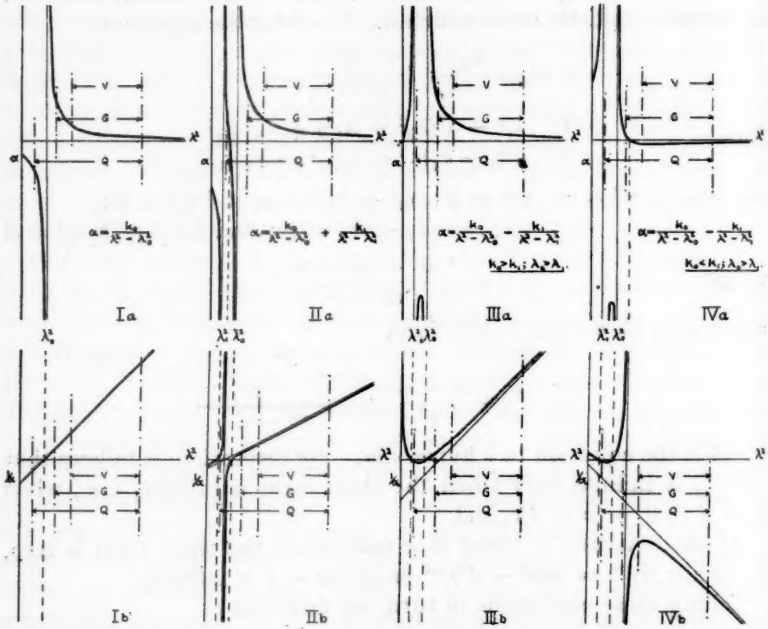
(*a*) $$\lambda^2 = \frac{k_0{\lambda_1}^2 + k_1{\lambda_0}^2}{k_0 + k_1}$$

and

(*b*) $$\frac{1}{\alpha} = \frac{\lambda^2}{k_0 + k_1} + \frac{k_0{\lambda_1}^2 + k_1{\lambda_0}^2 - ({\lambda_0}^2 + {\lambda_1}^2)(k_0 + k_1)}{(k_0 + k_1)^2}.$$

An examination of the curves shows that the main factor governing the amount of their departure from linearity in the region of the spectrum available to experimental observation is the position of asymptote (a). But this is nothing more than the criterion for the reversal of sign which was given by Lowry (J., 1915, **107**, 1195). It is therefore apparent that the curvature of the graph of $1/\alpha$ and λ^2 will be most marked when $(k_0\lambda_1^2 + k_1\lambda_0^2)/(k_0 + k_1)$ is large, and less so when this function is small. In other words, this method

FIG. 1.



The portions of the curves between the chain dotted lines indicate the regions of the spectrum experimentally available under the conditions specified: V = visually; G = photographically with glass optical parts; Q = photographically with quartz.

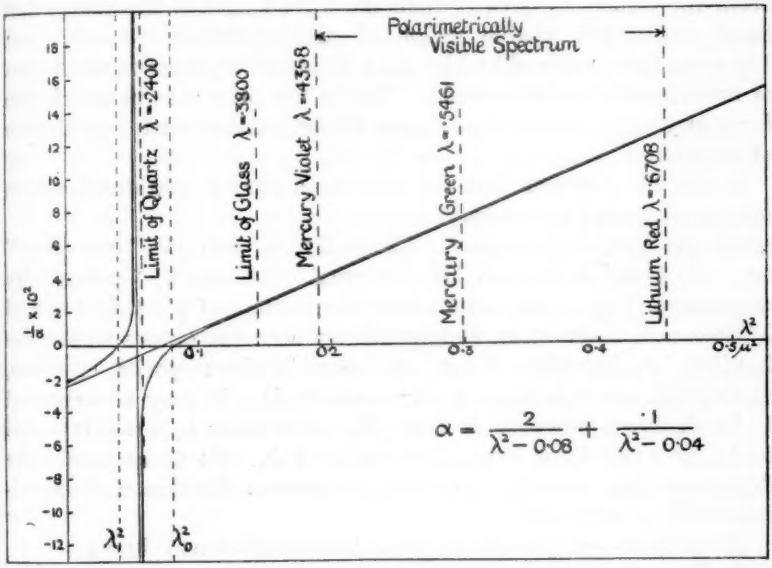
CURVES ILLUSTRATING THE DRUDE EQUATION.

is one which gives its most sensitive indications in cases of potentially anomalous dispersion. It should, however, differentiate between simple and all cases of complex rotatory dispersion if experimental measurements can be carried out over a sufficiently extended region of the spectrum. Unfortunately, this imposes a serious limitation on the method. Reference to the curves in Figs. 2 and 3 (Cases II and III, Fig. 1) shows that there is a slight, but perfectly distinct departure of the curve from linearity as the first absorption band is approached from the region of greater wave-length. This region, however, is inaccessible to experimental observation. Although the

rotatory power increases rapidly with decreasing wave-length, the substance becomes increasingly opaque as the band is approached, and thus polarimetric measurement becomes difficult, and finally impossible.

The treatment so far has been quite general, and it now becomes expedient to consider some special cases. Four such cases arise, and they are treated graphically in Fig. 1. It will be obvious, both from the foregoing and from the figures, that the curve obtained by plotting $1/\alpha$ and λ^2 must pass through the value zero when α becomes infinite, and, what is more important from the point of

FIG. 2.



view of this discussion, must pass through an infinite value whenever α becomes equal to zero. This condition enables us immediately to fix the position of one of the asymptotes to the $1/\alpha$–λ^2 curve for all cases.

Case I.—$\alpha = k_0/(\lambda^2 - \lambda_0{}^2)$. α never assumes a zero value for a finite value of λ, and the $1/\alpha$–λ^2 curve is linear, cutting the axis when $\lambda = \lambda_0$.

Case II.—$\alpha = k_0/(\lambda^2 - \lambda_0{}^2) + k_1/(\lambda^2 - \lambda_1{}^2)$. In this case the dispersion cannot become anomalous for any value of λ greater than the wave-length of the ultra-violet rotatory absorption band of greater wave-length. $\alpha = 0$ and $1/\alpha = \infty$ for a value of λ intermediate between λ_0 and λ_1. As it is impossible, with the experimental means at present at our disposal, to measure α in the

neighbourhood of λ_0 or λ_1, it will be impossible to detect the departure from linearity of the curve obtained by plotting $1/\alpha$ and λ^2 (see Fig. 2).

**Case III.*—$\alpha = k_0/(\lambda^2 - \lambda_0^2) - k_1/(\lambda^2 - \lambda_1^2)$, and $k_0 > k_1$, when $\lambda_0 > \lambda_1$. In this case the dispersion cannot become anomalous for any value of λ greater than the wave-length of the rotatory absorption band of shorter wave-length. $\alpha = 0$ and $1/\alpha = \infty$ for a value of λ less than λ_1, and it will be possible only in rare cases to detect the two terms in the equation (see Fig. 3).

Case IV.—$\alpha = k_0/(\lambda^2 - \lambda_0^2) - k_1/(\lambda^2 - \lambda_1^2)$, and $k_0 < k_1$, when $\lambda_0 > \lambda_1$. This is the only case in which anomalous dispersion can occur for values of λ greater than the wave-length of the absorption band nearer the visible region of the spectrum. $\alpha = 0$, and $1/\alpha = \infty$ for a value of λ which may lie in, or very near to, the region of experimental measurement. This is the only case in which the form of the dispersion curve may be determined with any degree of confidence.

It will be observed that the dispersion curves considered above may be classified in two ways:
either (*a*) Case I, "simple"; Cases II, III, and IV, "complex,"
or (*b*) Cases I, II, and III, "normal"; Case IV, "potentially anomalous." It is submitted that the method of plotting $1/\alpha$ and λ^2 does not, in practice, distinguish between the classes under the heading (*a*), but that it can, and does in the majority of cases, distinguish between those under heading (*b*). It may be expected to break down, however, in Case IV, either when λ_0 is nearly equal to λ_1, or when k_0 is very different from k_1. In these cases, the departure from linearity of the $1/\alpha$–λ^2 curve in the region of experiment will be very slight.

From these considerations, then, two conclusions follow:

(i) Since there is at present no criterion which can be applied to distinguish with certainty between simple and complex rotatory dispersion, this classification of dispersion must be abandoned.

(ii) In view of the fact that substances with rotatory dispersive

* The legitimacy of discussing the cases in which the terms are of opposite sign has been called into question by Baly (*loc. cit.*), who takes the view that the operation Σ cannot be read to include a difference. Apart from the fact that the mathematical term "sum" embraces "difference," there is a real difference between the physical significance of Σ as used in the Sellmeier and in the Drude equations. In the former equation, negative terms do not appear, because refractive index is a velocity ratio which cannot be imaginary unless selective reflection is to occur. Rotatory power, on the other hand, is essentially polar, and the sign of the rotation introduced by each term of the Drude equation must be considered. In other words, refractive index is a scalar quantity, whilst rotatory power is a vector

powers falling under Cases I, II, and III have hitherto been placed in the class of simply dispersing compounds, it now becomes necessary to revise our views on the chemical significance of rotatory dispersion. This second conclusion must be examined more fully, since it is the chemical aspect of rotatory dispersion which is of primary importance in this series of investigations.

The occurrence of anomalous rotatory dispersion has been ascribed to one or more of the following three causes (compare Tschugaev, *Trans. Faraday Soc.*, 1914, **10**, 28). It may be due to :

(*a*) the presence in the absorption spectrum of the substance of two (or possibly more) bands, each of which corresponds to one term of the Drude equation,

(*b*) the superposition of the partial rotations of two (or more) asymmetric centres within the molecule, each centre contributing its own term,

(*c*) the superposition of the rotations of two (or more) kinds of molecule in the medium, each of which has its own dispersion parameter.

If the dispersion is to be anomalous outside the range of wavelength included between the absorption bands or dispersion parameters, it is necessary that the rotation parameters associated with the two dispersion parameters shall be of opposite sign, whilst if it is to be anomalous on the visible side of the rotatory absorption bands, it is also necessary that the larger dispersion parameter be associated with the smaller rotation parameter. Of these three possible causes of anomalous dispersion, (*c*) has found most favour with workers in this field, whilst (*a*) has been almost entirely neglected, possibly because it is much less concrete than the other two.

It has been fairly generally accepted up to the present that complex or anomalous rotatory dispersion is nearly always caused by admixture of substances having different dispersive powers. This view must now be very considerably modified, if not abandoned altogether. There was never any theoretical justification for it; it was merely the most convenient of a number of alternative working hypotheses. Now, however, although it is not denied that substances may exist which exhibit simple rotatory dispersion,* we must not lose sight of the fact that a complex dispersion may simulate a simple one so closely that its true character escapes

* The whole of the evidence of absorption spectroscopy goes to show that compounds possessing only one absorption band do not exist. It is possible, however, that the complex absorption spectrum of an optically active compound may contain only *one* band controlling the *rotatory* dispersion, although *all* the bands must affect the *refractive* dispersion.

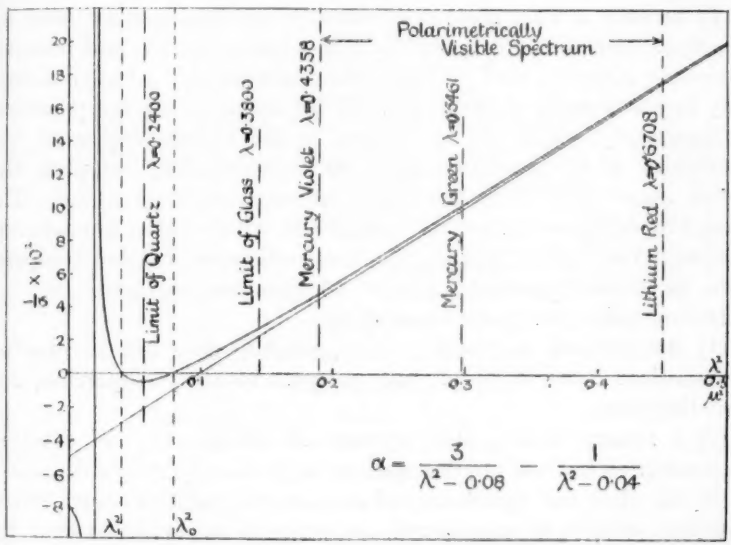
detection. It is therefore not improbable that most, if not all, of the compounds which have hitherto been considered to exhibit simple rotatory dispersion really show complex dispersion. The number of apparently homogeneous substances exhibiting complex rotatory dispersion is relatively small, and, up to the present, the postulation of dynamic isomerism of various types has sufficed to account for the optical heterogeneity of which the complex dispersion is symptomatic. If, however, dynamic isomerism is postulated to explain Case IV, we are logically bound to admit its occurrence in Cases II and III. Sooner or later, therefore, we may have to extend very considerably the list of substances suspected of exhibiting dynamic isomerism, and we may be led to an impasse where chemical evidence conflicts with physical ideas. In such a case we must be prepared to abandon or to modify the physical ideas. This possibility is by no means a remote one. Already, in Part VI of these investigations (J., 1914, **105**, 1115) there is the example of methyl-*tert.*-butylcarbinol which, in the early days of the work, was considered to show simple rotatory dispersion. The published figures show, however, distinct signs of complexity of dispersion, although there appears to be no plausible chemical mechanism by which dynamic isomerism could occur in this compound. In Part XXIII of this series will be described some ethers derived from optically active ethyl-*n*-hexylcarbinol which undoubtedly exhibit complex rotatory dispersion. Here, again, it is difficult to conceive of the existence of dynamic isomerides of these compounds, whilst in none of the cases can the optical properties be ascribed to the occurrence of phenomena of dissociation or association.

So far, we have considered only the difficulties with which we are confronted by adhering to the simple–complex system of classification and to the postulation of dynamic isomerism as a cause of complex rotatory dispersion. Let us now consider how far a return to a modified form of the normal–anomalous system would clear up some debatable points in the experimental evidence available. Although the study of rotatory dispersion is not at present in a very well-defined state, it will perhaps be well to take up without prejudice a definite attitude in order to fix our ideas. The following views will therefore be adopted.

There is at present no evidence that simple rotatory dispersion exists. Whilst not excluding the possibility of its occurrence, therefore, we cannot accept it as a determining factor in any of our theories. We are thus left with three cases to consider: Case II, where the two terms of the Drude equation have the same sign; and Cases III and IV, where they are of opposite sign and differ

only in the relative magnitudes of k_0 and k_1. Cases II and III cannot at present be distinguished by dispersion measurements alone, but Case IV exists as a class by itself. Cases II and III, however, are definitely different with regard to their behaviour when the values of k_0 and k_1 are made to change. The effect of temperature on the position of the absorption bands of organic compounds is not well understood, but by analogy with emission spectra it is probably negligible. Change of rotatory power with temperature must therefore be ascribed, not to alterations in λ_0, λ_1, etc., but to changes in the values of k_0, k_1, etc.

FIG 3.



Consider the rotatory dispersion of a substance falling within Case II. The value of λ which makes $\alpha = 0$ must lie within the comparatively narrow region between λ_0 and λ_1, no matter how k_0 and k_1 may vary, provided always that they are of the same sign. The asymptote (b) must always intersect the λ^2 axis within the region between $\lambda_0{}^2$ and $\lambda_1{}^2$. Here we have to deal with an example of pseudo-simple rotatory dispersion, since any experimentally determined points will lie practically on the asymptote. The observed experimental values will then fit a one-term Drude equation with a value of $\lambda_0{}^2$ corresponding to the point of intersection of the asymptote with the axis of λ^2, and this point must of necessity remain appreciably constant for all values of k_0 and k_1. The dispersion ratio of this compound will therefore remain appreciably constant over

a range of temperature. Its dispersion within the region of experimental observation is always normal, and is apparently simple, although it is really complex. β-Octanol may be taken as a possible example of this class, and its dispersion may be represented by curves II*a* and II*b*, Fig. 1.

The behaviour of a compound the dispersion of which falls within Case III may, however, be entirely different. The dispersion within the spectral range experimentally attainable will nearly always appear simple. The region of anomalous dispersion will always lie on the short wave-length side of the absorption bands and therefore will be inaccessible, so long as k_0 is greater than k_1 when λ_0 is greater than λ_1. Change of temperature, however, may alter k_0 with respect to k_1 in such a way that k_0 eventually becomes smaller than k_1. The dispersion then automatically falls within Case IV, and becomes obviously complex, and perhaps even anomalous. β-Octyl acetate may be an example of this type : its dispersion at low temperatures is apparently simple (at all events in the visible region of the spectrum), at temperatures above 40° it is definitely complex, and above about 140° it is anomalous in the visible spectrum. The 1-naphthylalkylcarbinols are examples in which rising temperature has the reverse effect, causing anomalous dispersion at low temperatures to become apparently simple at higher temperatures.

In conclusion, it is pointed out that—

(1) the method of plotting $1/\alpha$ against λ^2 does not in practice differentiate between simple and complex rotatory dispersion, and that therefore,

(2) a return to the older system of classification of rotatory dispersion as normal and anomalous is eminently desirable, and

(3) the chemical significance of a one-term and a two-term Drude equation cannot be considered, as we have no evidence that the former ever applies to organic compounds, but that

(4) there may be a chemical significance in the similarity or the dissimilarity of sign of the terms of the Drude equation, and finally,

(5) if these conclusions are accepted, dynamic isomerism is not a sufficient explanation of the optical heterogeneity which gives rise to complex and anomalous rotatory dispersion.

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